Supporting information

N-Monofluoromethoxy Benzoimidazole: A Bench Stable Reagent for Direct Radical Monofluoromethoxylation of Alkenes

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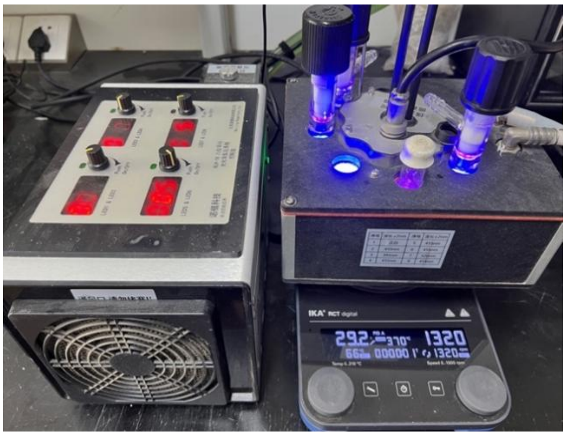
1. General information

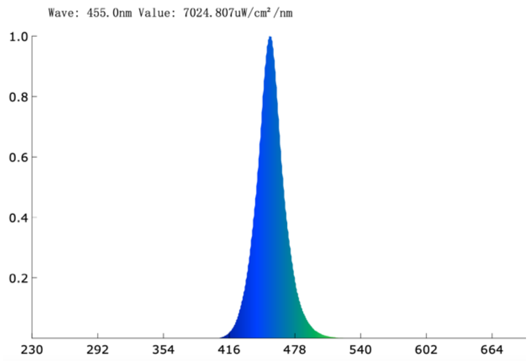
General Experimental. Unless otherwise noted, all reactions were carried out under argon atmosphere in a glass tube with magnetic stirring. Analytical thin layer chromatography (TLC) was performed with EM Science silica gel 60 F254 aluminum plates. Visualization was performed under a UV lamp (254 nm). Organic solutions were concentrated by rotary evaporation at 23-35 °C. Purification of products were generally carried out by flash column chromatography with 200-300 mesh silica gel.

Materials. Diarylketones, acetophenones, phenols, photocatalysts were purchased from Leyan.com, Bide Pharmatech Ltd. and Energy Chemical and used as received. Anhydrous solvents were purchased from J&K Scientific. Unless otherwise noted, all reagents were obtained commercially and used without further purification.

Instrumentation. Proton nuclear magnetic resonance spectra (^{1}H NMR) spectra, carbon nuclear magnetic resonance spectra (^{13}C NMR) and fluorine nuclear magnetic resonance spectra (^{19}F NMR, decoupled) were recorded at 23 °C on a Bruker 400 spectrometer in $CDCl_3$ or DMSO-d_6 (400 MHz for ^{1}H and 101 MHz for ^{13}C and 376 MHz for ^{19}F), and Bruker 600 spectrometer in $CDCl_3$ (151 MHz for ^{13}C). Chemical shifts for protons were reported as parts per million in δ scale using solvent residual peak ($CHCl_3$: 7.26 ppm; DMSO-d_6: 2.50 ppm) or tetramethylsilane (0.00 ppm) as internal standards. Chemical shifts of ^{13}C NMR spectra were reported in ppm from the central peak ($CDCl_3$: 77.16 ppm; DMSO-d_6: 39.52 ppm) on the δ scale. Chemical shifts of ^{19}F NMR spectra were reported in ppm using trifluorobenzene (-62.72 ppm) as internal standard. Data are represented as follows: chemical shift, integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), and coupling constant (J, Hz). High resolution mass spectra (HRMS) were obtained on a Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer using electron spray ionization (ESI). GC-MS spectra were recorded on Agilent Intuvo 9000/5977B GC/MS using electron ionization (EI) source. EPR was performed on a Bruker A300. X-ray data for the compound was collected at room temperature on a XtaLAB Synergy-DS instrument with a Cu microsource (λ = 1.54184 Å) and a hybrid photon counting detector.

The photochemical reactions were carried out under visible light irradiation by a blue LED at room temperature under argon atmosphere. RLH-18 8-position Photo Reaction System was manufactured by Beijing Roger Tech Ltd. (website: http://www.rogertech.cn/index.asp). Eight 50 W blue LEDs were equipped in this photoreactor (Figure S1). Reaction vessel is a borosilicate glass test tube, to which blue light is irradiated through a high-reflection channel (path length = 2 cm). There is no filter between LEDs and test tubes.





Parameter

Name	Value	Name	Value	Name	Value	Name	Value
ESuv(mW/cm²)	0.0000	SDCM	100.00	Peak Signal	52647		
Euvc(mW/cm²)	0.0000	Ra	-66.7	Dark Signal	2059		
Euvb(mW/cm²)	0.0000	Ee(mW/cm²)	207.55501	Compensate level	2876		
Euva(mW/cm²)	0.0000	S/P	21.279				
Euv(mW/cm²)	0.00	Dominant(nm)	459.10				
Eb(mW/cm²)	206.12	Purity(%)	98.9				
Eg(mW/cm²)	1.24	HalfWidth(nm)	25.0				
Er(mW/cm²)	0.00	Peak(nm)	455.6				
Eir(mW/cm²)	0.00	Center(nm)	455.2				
E(lx)	84980.54	Centroid(nm)	456.1				
Candle E(fc)	7894.88	Color Ratio(RGB)	0.0,9.6,90.4				
CCT(K)	100000	CIE1931 X	579283.125				
Duv	-0.06093	CIE1931 Y	124422.453				
CIE x,y	0.1475,0.0317	CIE1931 Z	3222999.500				
CIE u,v	0.1913,0.0616	TLCI-2012	1				
CIE u',v'	0.1913,0.0924	Integral Time(ms)	0.1				

CIE1931

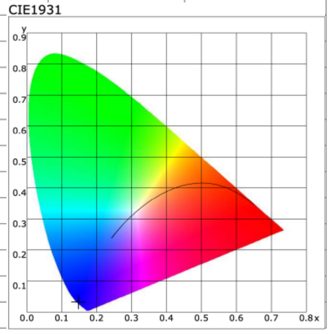
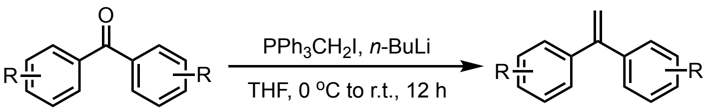


Figure S1. The photoreaction device

2. General procedures for the synthesis of substrates

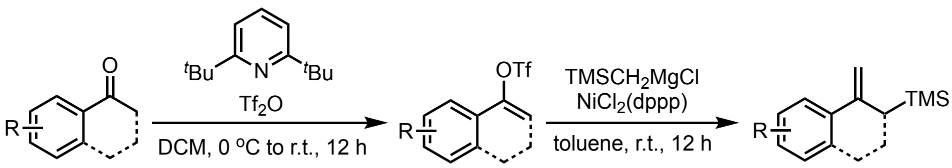
(1) General procedures (**A**) for the preparation of 1,1-disubstituted styrenes



To a round-bottom flask was added PPh_3CH_2I (7.5 mmol, 1.5 equiv.) purged with argon followed by the addition of anhydrous THF (20 mL). The reaction mixture was then cooled to 0 °C, and *n*-BuLi (7.5 mmol, 1.5 equiv. 1.6 M) was added dropwise. The reaction mixture was kept at this temperature for 30 mins and ketones (5.0 mmol, 1.0 equiv.) was added subsequently. The resulting mixture was warmed to room temperature and stirred for 12 h. Sat. NaCl was added to the mixture to quench the reaction and the solution was extracted with EtOAc. The separated organic solvent was dried over Na_2SO_4, filtered, and evaporated, and the resulting residue was purified by column chromatography on silica gel to afford the desired 1,1-disubstituted styrenes **S4-S20, S44-S47**.

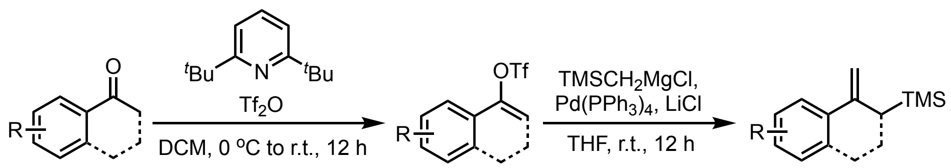
(2) General procedures (**B**) for the preparation of allylsilanes[1]

Method I:



To a solution of acetophenone (5.0 mmol, 1.0 equiv.) in DCM at 0 °C was added 2,6-di-*tert*-butylpyridine (6.0 mmol, 1.2 equiv.) and Tf_2O (6.5 mmol, 1.3 equiv.) sequentially. The reaction mixture was warmed to room temperature and stirred for 12 h. and then concentrated in vacuo. *n*-Hexane was added to the residue and the precipitate was filtered off. The filtrate was washed with cold HCl solution (1 M) and brine subsequently, dried over anhydrous Na_2SO_4. After concentration in vacuo, the resulting vinyl triflate was used for the next step without further purification. The residue was dissolved in anhydrous toluene and $NiCl_2$(dppp) (0.25 mmol, 5 mol%) was added to the solution under argon atmosphere. To the mixture was added a solution of (trimethylsilylmethyl)magnesium chloride in THF (1.3 M, mL, 7.5 mmol, 1.5 equiv.) dropwise and the reaction mixture was continued stirring at room temperature for 12 h. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (hexane: Et_3N = 1000: 1) to afford the desired allysilanes **S27**, **S28**, **S29**, **S30**, **S31**, **S34**, **S36**, **S37**, **S38** and **S40**.

Method II:

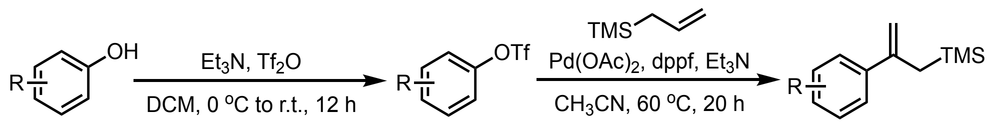


To a solution of acetophenone (5.0 mmol, 1.0 equiv.) in DCM at 0 °C was added 2,6-di-*tert*-butylpyridine (6.0 mmol, 1.2 equiv.) and Tf_2O (6.5 mmol, 1.3 equiv.) sequentially. The reaction mixture was warmed to room temperature and stirred for 12 h. and then concentrated in vacuo. *n*-Hexane was added to the residue and the precipitate was filtered off. The filtrate was washed with cold HCl solution (1 M) and brine subsequently, dried over anhydrous Na_2SO_4. After concentration in vacuo, the resulting vinyl triflate was used for the next step without further purification. The residue was dissolved in anhydrous toluene and $Pd(PPh_3)_4$ and LiCl (10 mmol,

[1] (a) Y. Liu, H. Li, S. Chiba, *Org. Lett.* **2021**, *23*, 427-432; (b) H.Teare, E. G. Robins, E. Årstad, S. K. Luthra, V. Gouverneur, *Chem. Commun.* **2007**, 2330-2332.

2.0 equiv.) was added to the solution under argon atmosphere. To the mixture was added a solution of (trimethylsilylmethyl)magnesium chloride in THF (7.5 mmol, 1.5 equiv., 1.3 M) dropwise and the reaction mixture was continued stirring at room temperature for 12 h. The reaction mixture was quenched with saturated aqueous solution of NH_4Cl and extracted with EtOAc. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and concentrated in vacuo. The crude product was purified by flash chromatography on silica gel (hexane: Et_3N = 1000: 1) to afford the desired allysilanes **S23**, **S24**, **S25**, **S39**, **S41**, **S42** and **S44**.

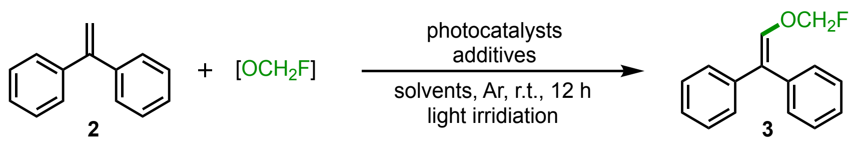
<u>Method III:</u>



To a solution of phenols (5.0 mmol, 1.0 equiv.) in DCM at 0 °C was added Et_3N (6.0 mmol, 1.2 equiv.) and Tf_2O (6.5 mmol, 1.3 equiv.) sequentially. The reaction mixture was warmed to room temperature and stirred for 12 h. Then, H_2O was added to quench the reaction and extracted with EtOAc. The separated organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The resulting crude product was purified by column chromatography (hexane: EtOAc = 100: 1) to give the product. Treatment of phenyl triflate (2.0 mmol, 1.0 equiv.), $Pd(OAc)_2$ (0.06 mmol, 0.03 equiv.), dppf (0.26 mmol, 0.13 equiv.), allyltrimethyl silane (10.0 mmol, 5.0 equiv.), Et_3N (4.0 mmol, 2.0 equiv.) and anhydrous CH_3CN (10 mL) in a round-bottom flask, and then the solution was heated at 60 °C for 20 h. The reaction mixture was cooled to room temperature, quenched with water and extracted with EtOAc. The separated organic layers were evaporated to dryness and then purified by column chromatography on silica gel to provide the desired product **S26**, **S33**, **S35**, **S49**, **S50**, **S51**, **S52** and **S53**.

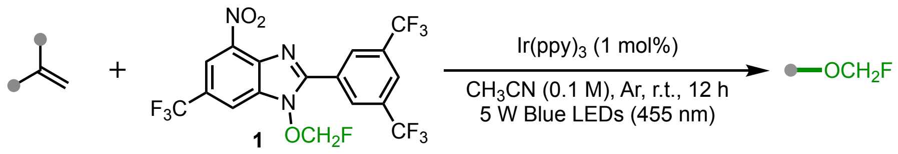
3. General procedures for monofluoromethoxylations

(1) General procedure (**C**) for optimizations to preparing product **3**



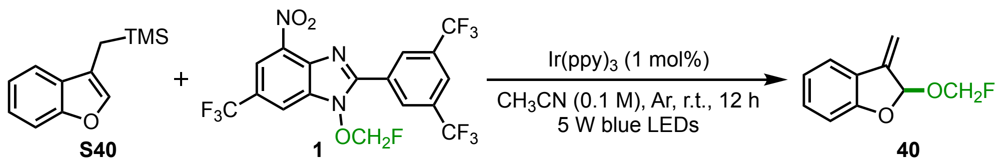
To a glass tube equipped with a magnetic stir bar was diphenyl ethylene **2** (0.2 mmol, 2.0 equiv.), OCH_2F reagent (0.1 mmol, 1.0 equiv.), photocatalyst (x mol%), additives (1.0 ~ 2.0 equiv.), and solvent (x mL). The reaction was allowed to stir at room temperature for 12 h under light irradiation with argon atmosphere. Aliquots were taken from the tube for yields measurements by GCMS with diethyl phthalate as internal standard.

(2) General procedure (**D**) for the monofluoromethoxylation of allysilanes to preparing products **3-53**



To a glass tube equipped with a stir bar was charged alkenes (0.4 mmol, 2.0 equiv.), **1** (0.2 mmol, 1.0 equiv.), Ir(ppy)3 (1 mol%), CH_3CN (2 mL). The reaction mixture was allowed to stir at room temperature for 12 h under 5W blue LEDs irradiation with argon atmosphere. The suspension was diluted with EtOAc and washed with water. The combined separated organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the resulting crude was purified by column chromatography on silica gel (hexane/EtOAc) to afford the desired monofluoromethoxylated product **3**-**53**.

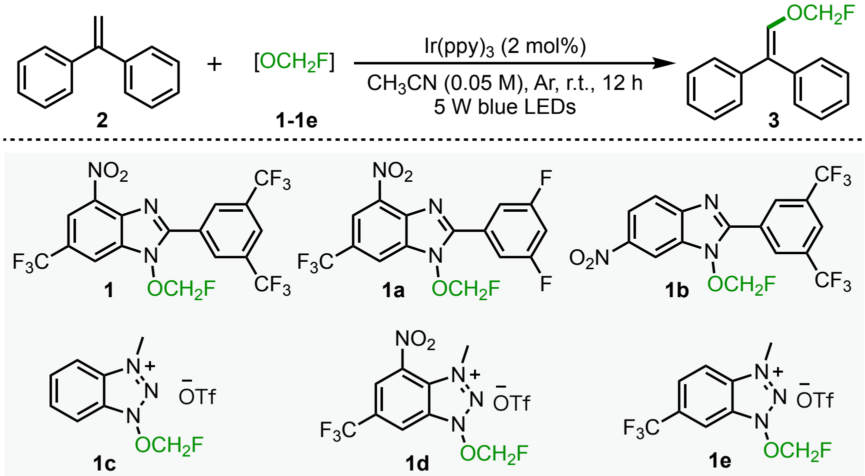
(3) Scale-up synthesis of the product **40**



To a glass tube equipped with a stir bar was charged **S40** (4.0 mmol, 2.0 equiv.), **1** (2.0 mmol, 1.0 equiv.), Ir(ppy)3 (1 mol%), CH_3CN (20 mL). The reaction mixture was allowed to stir at room temperature for 12 h under 5W blue LEDs irradiation with argon atmosphere. The suspension was diluted with EtOAc and washed with water. The combined separated organic layers were dried over anhydrous Na_2SO_4, concentrated under reduced pressure and the resulting crude was purified by column chromatography on silica gel (hexane/EtOAc =100： 1) to afford compound **40** as yellow oil (234.1mg, 65% yield).

4. Optimization studies for the formation of 3

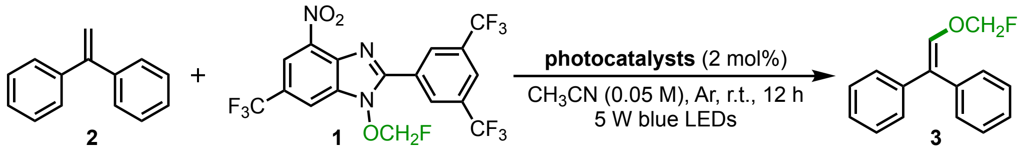
Table S1. [OCH_2F] reagent screening.[a]



Entry	[OCH_2F] sources	GC yield[b]
1	**2a**	**36%**
2	2b	11%
3	2c	<5%
4	2d	14%
5	2e	N. R.[c]
6	2f	24%

[a]Reaction conditions: **2** (0.3 mmol), **[OCH_2F] reagent** (0.1 mmol), Ir(ppy)$_3$ (2 mol%), CH_3CN (2 mL), r.t., Ar, 5W blue LEDs, 12 h; [b]Yields were determined by GCMS with diethyl phthalate as internal standard. [c]N. R.: no reaction.

Table S2. Optimizations of photocatalysts.[a]

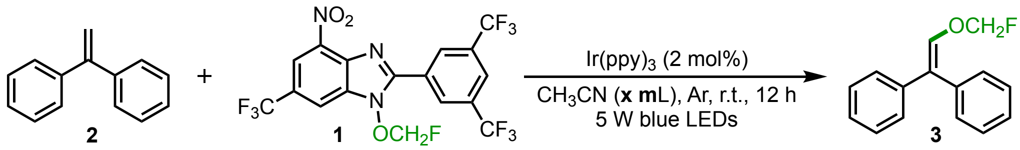


Entry	Photocatalysts	GC yield[b]
1	**$Ir(ppy)_3$**	**36%**
2	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	<5%
3	$Ir[dF(Me)ppy]_2(phen)PF_6$	N. R.[c]
4	$[Ir(dF\text{-}mppy)Cl]_2$	<5%
5	$[Ir(dF\text{-}CF_3\text{-}ppy)_2Cl]_2$	N. R.
6	Ir(*p*-CF_3-ppy)$_3$	35%
7	Ir(*p*-F(^{t}Bu)-ppy)$_3$	14%
8	Ir(*p*-^{t}Bu-ppy)$_3$	<5%
9	$[Ru(dtbbpy)_3](PF_6)_2$	N. R.
10	$Ru(bpy)_3(PF_6)_2$	10%
11	$Ru(phen)_3(PF_6)_2$	<5%
12	$Ru(phen)_3Cl_2{\cdot}H_2O$	14%
13	$Ru(bpy)_3Cl_2{\cdot}6H_2O$	16%
14	3CzEPAIPN[c]	<5%
15	4-CzIPN	N. R.
16	4DPAIPN	<5%
17	TBADT	<5%
18	AQDS	N. R.
19	di-^{t}Bu-Mes-$Acr^+BF_4^-$	N. R.
20	10-Phenyl-10H-phenothiazine (PTH)	N. R.
21	Rose bengal	<5%
22	Fluorescein	N. R.
23	Rhodamine B	N. R.
24	Rhodamine 6G	N. R.
25	2,4,6-Triphenylpyrylium tetrafluoroborate	<5%
26	Perylene	13%

27	Eosin Y	12%

[a]Reaction conditions: **2** (0.3 mmol), **1** (0.1 mmol), photocatalysts (2 mol%), CH_3CN (2 mL), r.t., Ar, 5W blue LEDs, 12 h; [b]Yields were determined by GCMS with diethyl phthalate as internal standard. [c]N. R.: no reaction.

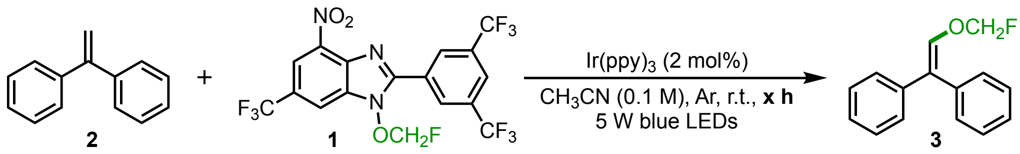
Table S3. Optimizations of concentration.[a]



Entry	CH_3CN (x mL)	GC yield[b]
1	0.5 mL (0.2 M)	41%
2	**1.0 mL (0.1 M)**	**51%**
3	2.0 mL (0.05 M)	36%
4	3.0 mL (0.033M)	17%
5	4.0 mL (0.025 M)	16%
6	5.0 mL (0.02 M)	9%

[a]Reaction conditions: **2** (0.3 mmol), **1** (0.1 mmol), $Ir(ppy)_3$ (2 mol%), CH_3CN (x mL), r.t., Ar, 5W blue LEDs, 12 h; [b]Yields were determined by GCMS with diethyl phthalate as internal standard.

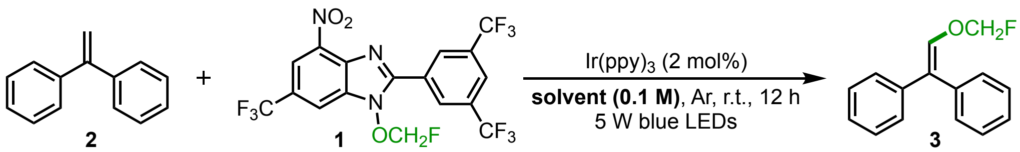
Table S4. Optimizations of reaction times.[a]



Entry	Reaction times	GC yield[b]
1	2 h	7%
2	5 h	35%
3	**12 h**	**51%**
4	24 h	50%

[a]Reaction conditions: **2** (0.3 mmol), **1** (0.1 mmol), $Ir(ppy)_3$ (2 mol%), CH_3CN (1 mL), r.t., Ar, 5W blue LEDs, x h; [b]Yields were determined by GCMS with diethyl phthalate as internal standard.

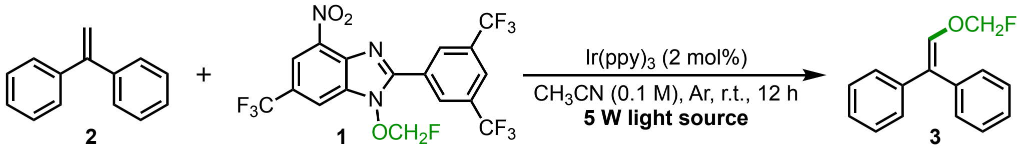
Table S5. Optimizations of solvents.[a]



Entry	Solvents	GC yield[b]
1	**CH_3CN**	**51%**
2	DCM	N. R.[c]
3	DMF	trace
4	THF	N. R.
5	Acetone	15%
6	MeOH	N. R.
7	DCE	trace
8	DMSO	N. R.
9	1,4-Dioxane	N. R.
10	MTBE	trace

[a]Reaction conditions: **2** (0.3 mmol), **1** (0.1 mmol), $Ir(ppy)_3$ (2 mol%), solvents (1 mL), r.t., Ar, 5W blue LEDs, 12 h; [b]Yields were determined by GCMS with diethyl phthalate as internal standard. [c]N. R.: no reaction.

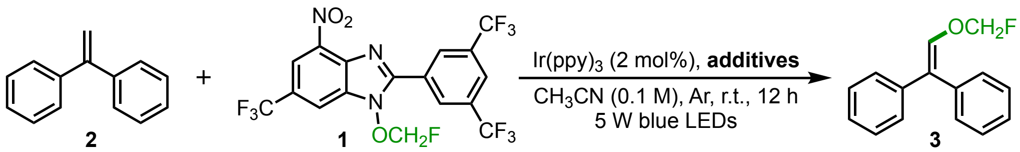
Table S6. Optimizations of light source.[a]



Entry	Light source	GC yield[b]
1	**Blue (455 nm)**	**51%**
2	Purple (390 nm)	trace
3	Green (520 nm)	N. R.
4	CFL	12%

[a]Reaction conditions: **2** (0.3 mmol), **1** (0.1 mmol), Ir(ppy)$_3$ (2 mol%), CH_3CN (1 mL), r.t., Ar, 5W light irridiation, 12 h; [b]Yields were determined by GCMS with diethyl phthalate as internal standard. [c]N. R.: no reaction.

Table S7. Optimizations of additives.[a]

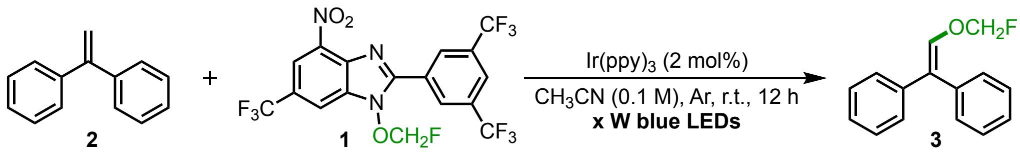


Entry	Additives (2.0 equiv.)	GC yield[b]
1	**-**	**51%**
2	$Na_2S_2O_8$	45%
3	$K_2S_2O_8$	48%
4	$(NH_4)_2S_2O_8$	36%
5	PIDA	trace
6	PIFA	trace
7	TBHP	trace
8	Oxone	49%
9	DDQ	N. R.
10	NFSI	15%
11	*m*-CPBA	12%
12	DIPEA	N. R.
13	TMEDA	N. R.

14	DMAP	N. R.
15	Proton sponge	N. R.
16	Cs_2CO_3	trace
17	DBU	N. R.
18	KO^{t}Bu	N. R.
19	2,6-Lutidine	N. R.

[a]Reaction conditions: **2** (0.3 mmol), **1** (0.1 mmol), $Ir(ppy)_3$ (2 mol%), additives (2.0 equiv.), CH_3CN (1 mL), r.t., Ar, 5W blue LEDs, 12 h; [b]Yields were determined by GCMS with diethyl phthalate as internal standard. [c]N. R.: no reaction.

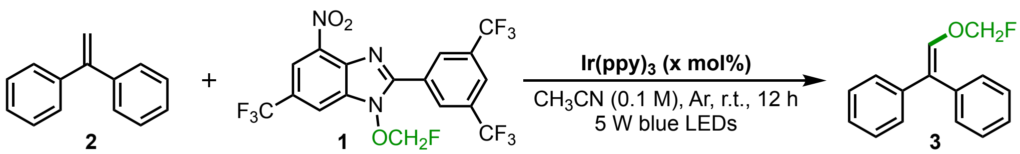
Table S8. Optimizations of light intensity.[a]



Entry	Light intensity	GC yield[b]
1	1W	15%
2	**5W**	**51%**
3	10W	17%
4	20W	5%
5	30W	2%
6	40W	N. R.[c]

[a]Reaction conditions: **2** (0.3 mmol), **1** (0.1 mmol), $Ir(ppy)_3$ (2 mol%), CH_3CN (1 mL), r.t., Ar, x W blue LEDs, 12 h; [b]Yields were determined by GCMS with diethyl phthalate as internal standard. [c]N. R.: no reaction.

Table S9. Screening of equivalents of catalyst.[a]



Entry	2 (x equiv.)	$Ir(ppy)_3$ (x mol%)	GC yield[b]
1	1	2	38%
2	2	2	50%
3	3	2	51%

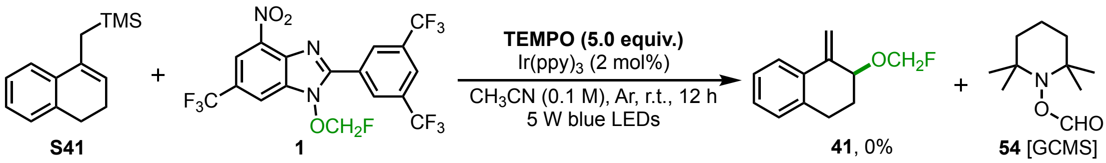
4	5	2	48%
5	3	2	62%
6	**2**	**1**	**68%**

[a]Reaction conditions: **2** (x mmol), **1** (0.1 mmol), $Ir(ppy)_3$ (x mol%), CH_3CN (1 mL), r.t., Ar, 5 W blue LEDs, 12 h; [b]Yields were determined by GCMS with diethyl phthalate as internal standard.

5. Mechanistic studies

(1) Radical trapping experiments

a. addition of TEMPO (5.0 equiv.) suppressed the transformation, and the desired product **41** was not obtained. Product of **54** was formed by the hydrolysis of TEMPO-OCH_2F was detected by GCMS analysis.



According to the general procedure **D**, allylsilane **S41** (0.2 mmol, 2.0 equiv.), **1** (0.1 mmol, 1.0 equiv.), $Ir(ppy)_3$ (1 mol%), TEMPO (0.5 mmol, 5.0 equiv.) and anhydrous CH_3CN (1.0 mL). The resulting suspension was stirred at room temperature under Ar atmosphere by 5W blue LEDs for 12 h. The reaction mixture was analyzed by GCMS with as the internal standard (Figure S1).

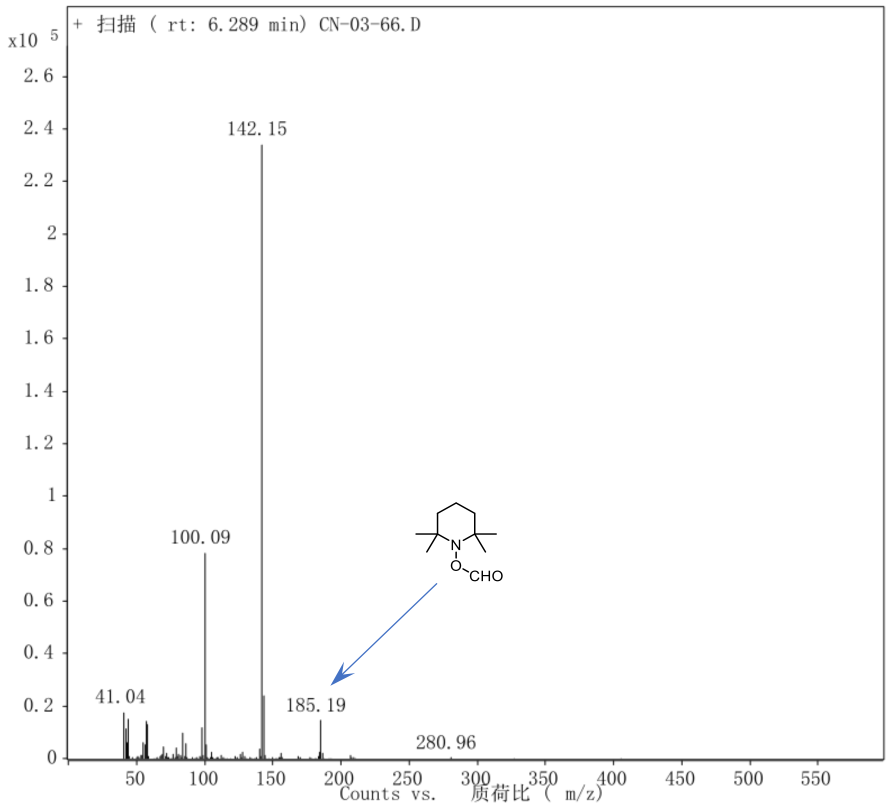
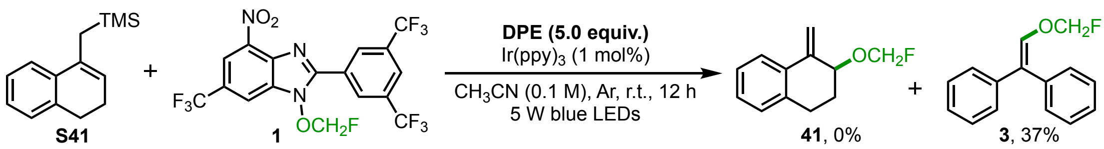


Figure S1. GCMS data of TEMPO-trapping experiment.

b. addition of DPE (5.0 equiv.) suppressed the transformation, and the desired product **41** was not obtained. DPE-trapped adduct **3** were isolated in 37% yield.



According to the general procedure **D**, allysilane **S41** (0.2 mmol, 2.0 equiv.), **1** (0.1 mmol, 1.0 equiv.), Ir(ppy)$_3$ (1 mol%), DPE (0.5 mmol, 5.0 equiv.) and anhydrous CH_3CN (1.0 mL). The resulting suspension was stirred at room temperature under Ar by 5W blue LEDs for 12 h. The reaction mixture was purified by column chromatography on silica gel.

c. addition of trimethyl phosphite P(OMe)$_3$ as a trap for OCH_2F radical led to the formation of trimethyl phosphate (OMe)$_3$P=O **56** based on ^{31}P NMR analysis, which attributed to the radical addition of OCH_2F to P(OMe)$_3$ followed by β-scission.

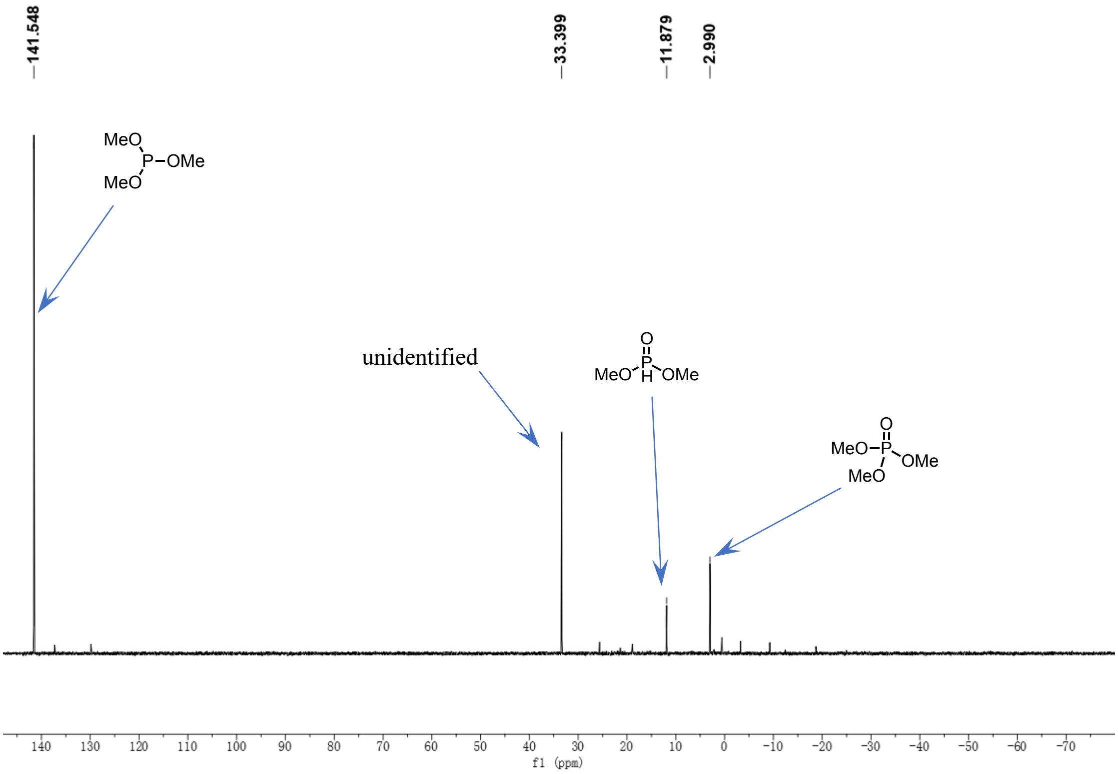


Figure S2. ^{31}P NMR of the crude reaction mixture.

According to the general procedure **D**, a reaction mixture of 1 (0.1 mmol, 1.0 equiv.), P(OMe)$_3$(0.5 mmol, 5.0 equiv.), Ir(ppy)$_3$ (1 mol%), and anhydrous CH_3CN (1 mL). The reaction mixture was allowed to stir at room temperature for 4 h under 5W blue LEDs irradiation and argon atmosphere in a photo-reactor. The reaction mixture was analyzed by ^{31} P NMR.

(2) EPR experiments

EPR spectra were recorded on a Bruker A300. Microcapillary with inner diameter 1 mm was used for analysis.

Procedure: In glovebox, to an oven-dried reaction tube equipped with OCH_2F reagent **1** (0.1 mmol, 1.0 equiv.), Ir(ppy)$_3$ (1 mol%), PBN (*N*-benzylidene-*tert*-butylamineoxide) or POBN (*N*-*tert*-butyl-alpha-(4-pyridyl-1-oxide), CH_3CN (1.0 mL) and a stir bar. The reaction mixture was brought out and stirred at room temperature for 0.5 h under 5 W blue LED irradiation with argon atmosphere and then rapid sampling analyzed by EPR (Figure S3-S4).

a. PBN as radical trap

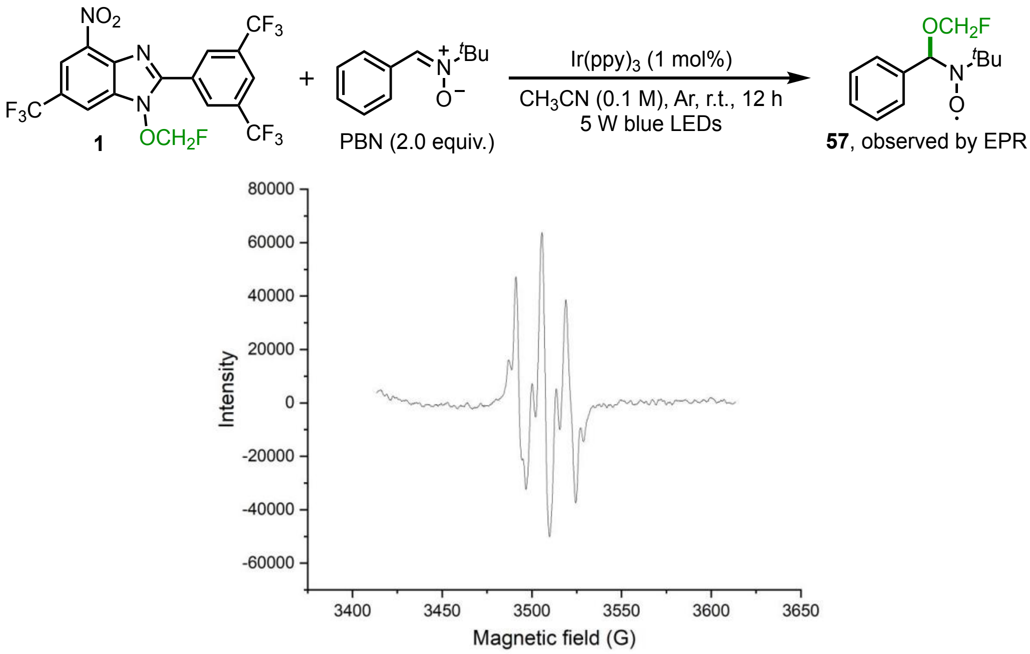


Figure S3. The EPR spectrum of the radical **57** (The EPR instrumental settings was as follows: field sweep, 200G; microwave frequency, 9.85 GHz; microwave power, 21.27 mW; modulation amplitude, 1.0 G; conversion time 15 ms; time constant, 1.28 ms; sweep time 61.44 s; receiver gain, 1×10^3; resolution, 4096 points.)

b. POBN as radical trap

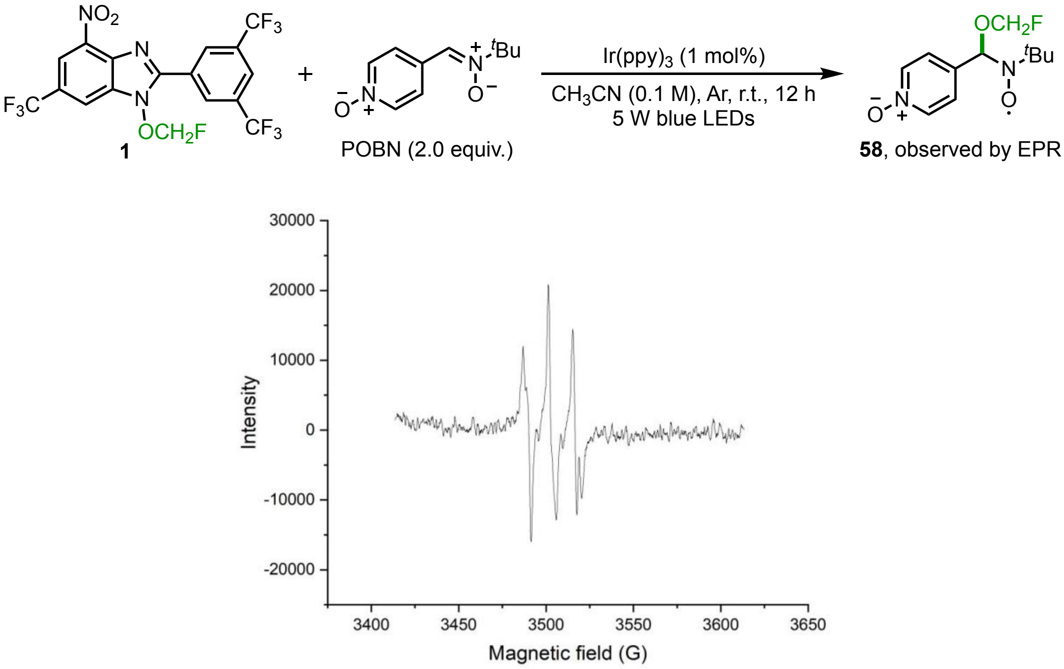
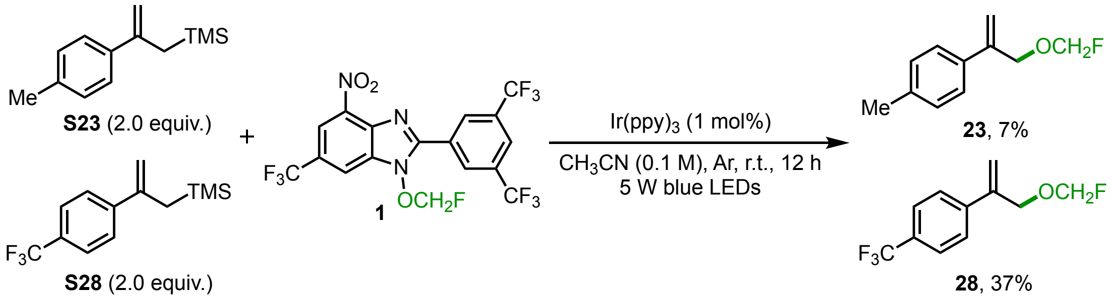


Figure S4. The EPR spectrum of the radical **58** (The EPR instrumental settings was as follows: field sweep, 200G; microwave frequency, 9.85 GHz; microwave power, 21.27 mW; modulation amplitude, 1.0 G; conversion time 15 ms; time constant, 1.28 ms; sweep time 122.88 s; receiver gain, 1×10^3; resolution, 8192 points.)

(3) Intermolecular competition experiments



According to the general procedure **D**, a reaction mixture of **S23** (0.2 mmol, 2.0 equiv.), **S28** (0.2 mmol, 2.0 equiv.), **1** (0.1 mmol, 1.0 equiv.), $Ir(ppy)_3$ (1 mol%) and anhydrous CH_3CN (2 mL). The reaction mixture was allowed to stir at room temperature for 12 h under 5 W blue LEDs irradiation and argon atmosphere. The reaction mixture was purified by column chromatography to provide the products.

28 was isolated as the major product, while **23** was obtained in trace amounts. Although OCH_2F radical has been reported to exhibit a electrophilic nature in the C-H monofluoromethoxylation reactions, the reactivity in the radical reaction with alkenes proceeded through a concerted mechanism or it involved discrete intermediates.

(4) Fluorescence quenching experiments (Stern-Volmer studies)

All fluorescence measurements were recorded using a Horiba jobin yvon FL3-p-TCSPC fluorometer. Stern-Volmer luminescence quenching studies were performed using a stock solution of the photocatalyst and variable concentrations of the potential quenchers at room temperature. All solutions of $Ir(ppy)_3$ in MeCN (concentration of 1×10^{-4} M) were excited at 425 nm and the emission intensity was collected at 519 nm (Figures S5-S7).

$Ir(ppy)_3$ (6.5 mg, 0.01 mmol) and **1** (5.0 mg, 0.01 mmol) were dissolved in 10.0 mL MeCN and dilute tenfold, respectively and stored in dark. For each quenching experiment, 5 μL of **1** was titrated each time to a solution (2.0 mL) of $Ir(ppy)_3$ in a cuvette. The addition of 5 μL stock solution refers to an increase of the quencher concentration of 2.5×10^{-7} M. I_0 is the luminescence intensity without the quencher, I is the intensity in the presence of the quencher. The results are listed below:

All fluorescence measurements were recorded using a Horiba jobin yvon FL3-p-TCSPC fluorometer. Stern-Volmer luminescence quenching studies were performed using a stock solution of the photocatalyst and variable concentrations of the potential quenchers at room temperature. All solutions of $Ir(ppy)_3$ in MeCN (concentration of 1×10^{-3} M) were excited at 425 nm and the emission intensity was collected at 519 nm (Figures S5-S8).

Ir(ppy)$_3$ (6.5 mg, 0.01 mmol), **1** (64.4 mg, 0.125 mmol), **2** (22 μL, 0.125 mmol), **S22** (27 μL, 0.125 mmol) were dissolved in 10.00 mL MeCN, respectively and stored in dark. For each quenching experiment, 5 μL of **1**, **2** or **S22** were titrated each time to a solution (2.0 mL) of Ir(ppy)$_3$ in a cuvette. The addition of 5 μL stock solution refers to an increase of the quencher concentration of 12.5 mM. I_0 is the luminescence intensity without the quencher, I is the intensity in the presence of the quencher. The results are listed below:

a. Fluorescence spectra of compound 1

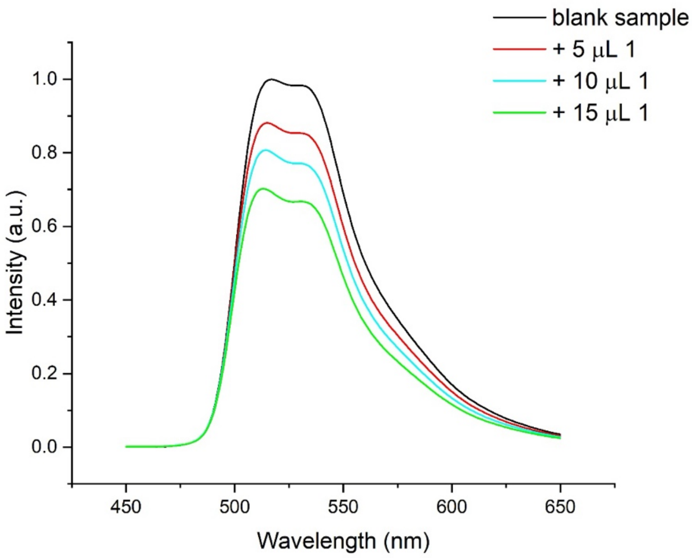


Figure S5. Fluorescence emission spectra of Ir(ppy)$_3$ in CH_3CN with different concentrations of **1** (concentration of 1.25*10^{-2} M). The excitation wavelength was 425 nm.

b. Fluorescence spectra of compound 2

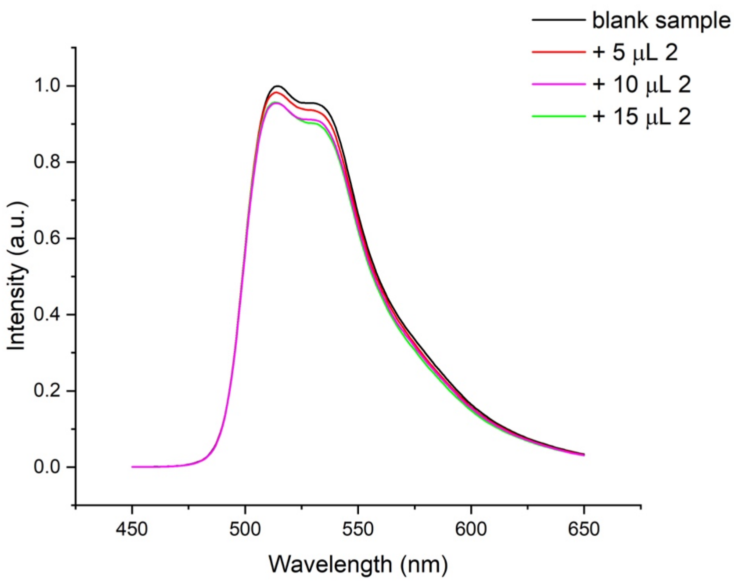


Figure S6. Fluorescence emission spectra of Ir(ppy)$_3$ in CH_3CN with different concentrations of **2** (concentration of 1.25*10^{-2} M). The excitation wavelength was 425 nm.

c. Fluorescence spectra of compound S22

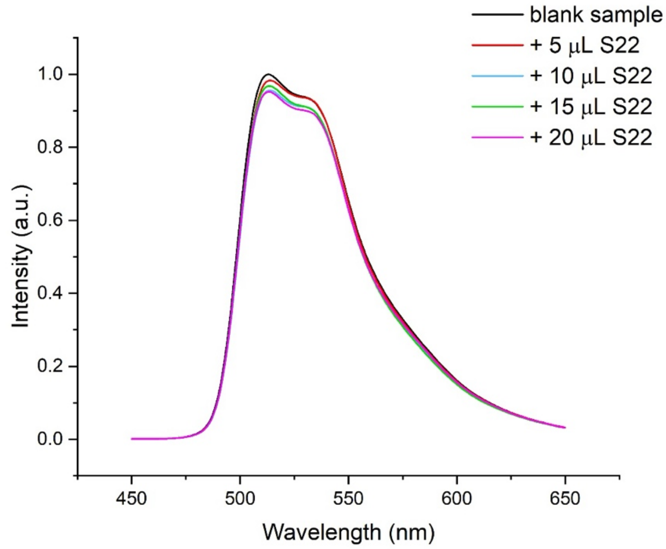


Figure S7. Fluorescence emission spectra of Ir(ppy)$_3$ in CH_3CN with different concentrations of **S22** (concentration of 1.25*10 $^{-2}$ M). The excitation wavelength was 425 nm.

Table S10. Result of Stern-Volmer fluorescence quenching.

Entry	1	2	3	4	5
Quencher C	0	3.12×10^{-5}	6.22×10^{-5}	9.13×10^{-5}	1.24×10^{-4}
I_0/I_1	1	1.1457	1.2595	1.4600	
I_0/I_2	1	1.0221	1.0476	1.0636	
I_0/I_3	1	1.0213	1.0358	1.0473	1.0531

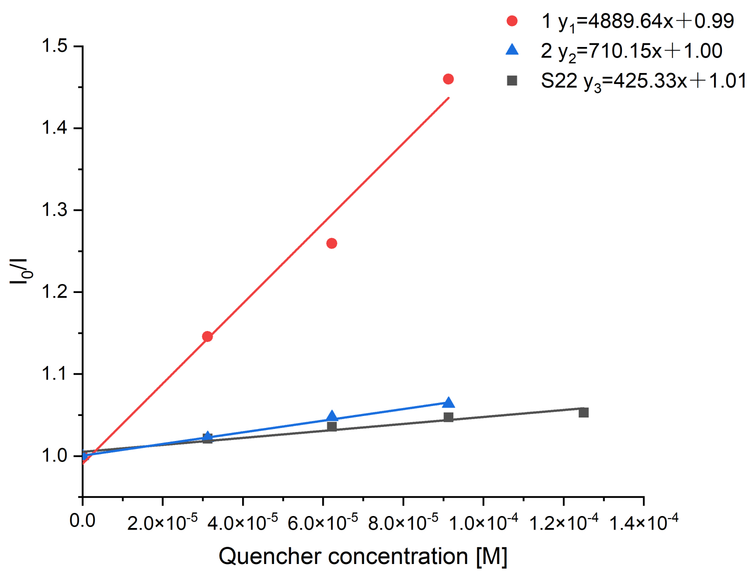


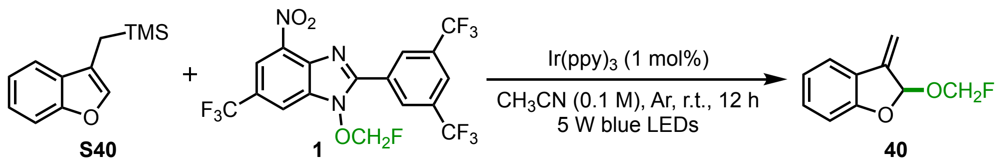
Figure S8. Stern-Volmer fluorescence quenching studies including **1, 2** and **S22**.

Comment on the data:

Stern-Volmer fluorescence quenching experiments reveal that reagent **1** is the quencher of the excited state of $Ir(ppy)_3$, whereas substrates **2** or **S22** exhibit only negligible quenching. This support the assumption that the intial step of the mechanism constitutes the radical generation of **1** by the photocatalyst.

(5) Light on/off experiments

Standard reactions were set up parallelly on a 0.1 mmol scale according to the general procedure **D** for the preparation of **40**. After each irradiation, the yield of **40** was determined via ^{19}F NMR analysis. The reaction was irradiated with blue LEDs and kept in the dark in 2 h intervals at room temperature. The white area represents the light irradiation, while the yellow area indicates time light-off. The reaction proceeded smoothly under the irradiation of blue LEDs, but no further transformation was observed without the light irradiation, showcasing that light is a necessary component for this catalytic reaction.



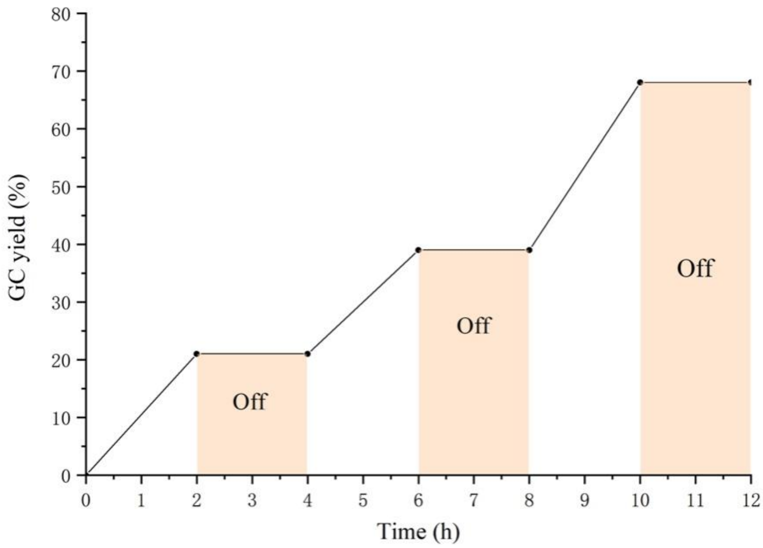


Figure S9. ^{19}F NMR yields line chart of compound **40** in light on-off experiments.

(6) Reaction sensitivity experiments

The sensitivity screen was performed according to the established method by the Glorius group to investigate the tolerance and generality of the standard condition to the unoptimized conditions.

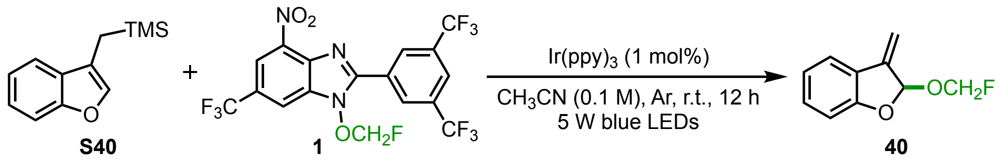


Table S11. Results of the sensitivity screen for monofluoromethoxylation reaction. All reactions were performed on 0.1 mmol scale. Only entry 11, was conducted at 2.0 mmol scale; where *n* signifies 0.1 mmol.

Entry	Experiment	Notes	Relative difference in yield(%)	^{19}F NMR yield (%)
1	High concentration	-100 µL CH_3CN	0	75
2	Low concentration	+100 µL CH_3CN	-3	75
3	High H_2O	+20 µL H_2O	-9	66
4	Low H_2O	+2 µL H_2O	-7	68
5	Low O_2	Under Ar	0	75
6	High O_2	Under Air	-71	4
7	Low T	- 10℃ (20 ℃)	-1	74
8	High T	+ 10℃ (40 ℃)	-7	68
9	Low I	- 4 W	-54	54
10	High I	+ 4 W	-21	21
11	Big Scale	2 mmol	-10	65

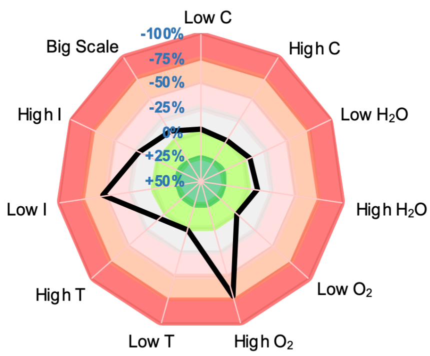


Figure S10. Radar diagram of the sensitivity screen for the reaction.

Comment on the data:

As depicted from the results of Table S11 and the radar diagram Figure S10, we observed a slightly reduction of the yield in the case of concentration, the effect of water, temperature, as well as big scale reaction, however, a comparable negative effect was observed in the manipulation of the light intensity. Noticeably, high-oxygen infestation shut down the reaction completely.

6. Cyclic voltammetry studies of 1

Cyclic voltammetry measurement was recorded on a CHI 660E potentiostat at room temperature (25 °C). The CV plotting convention is IUPAC. The initial potential: 0 V, the direction of initial scan: reductive. Scan rate: 100 mV/s. The three-electrode system was used with a platinum wire as the counter electrode, a glassy carbon disk (diameter, 3 mm) was used as the working electrode, and Ag/AgCl in 1.0 M KCl electrode was used as the reference electrode. Sample was prepared with 0.5 mmol of **1** in 10 mL of 0.1 M $LiClO_4$ in dry CH_3CN. The obtained value was referenced to Ag/Ag^+. (Figure S11).

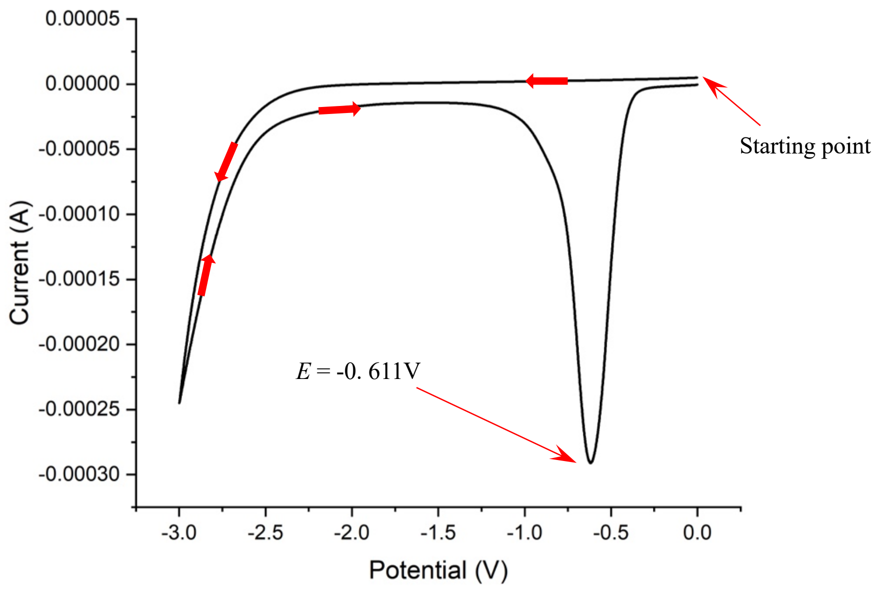


Figure S11. Cyclic voltammetry of **1** in 0.1 M $LiClO_4$ of CH_3CN; CV plotting convention: IUPAC; Working electrode: carbon disk; Counter electrode: platinum; Reference electrode: Ag/AgCl (1.0 M in KCl); Init E (V) = 0 V, High E (V) = 0 V, Final E (V) = 0 (V).

7. Thermogravimetric and Differential scanning calorimetry analysis (TG-DSC) of reagent 1

The thermogravimetric and differential scanning calorimetry analysis (TG-DSC) was performed with Netzsch STA 409PC. Heating of the samples from 30 °C to 400 °C was performed at a 10 °C/min heating rate. Sample of 5.98 mg mass were used, and the nitrogen flow rate was 50 mL/min.

TG-DSC analysis revealed that a exothermic decomposition of reagent **1** was observed above 200 °C, which would also match with the determined melting point (202 - 204°C).

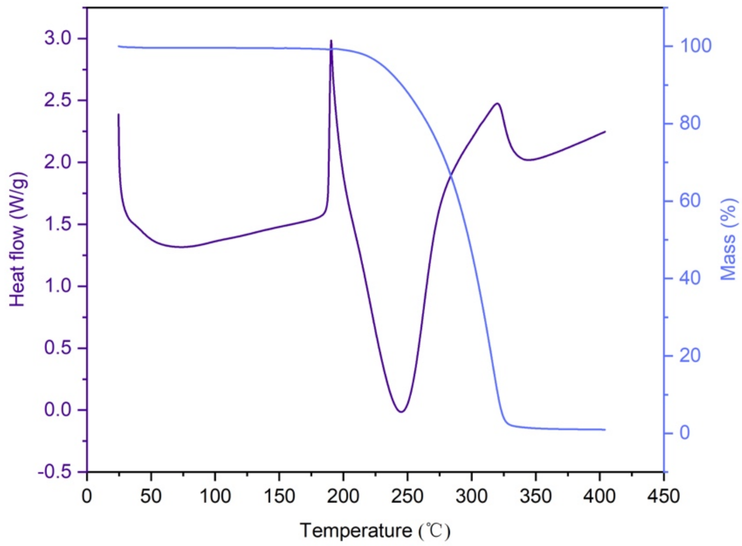
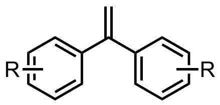


Figure S12. TG and DSC curve of reagent **1**.

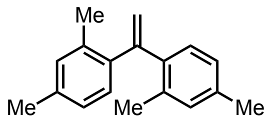
8. Starting materials used in the scope table

A. 1,1-disubstituted alkenes

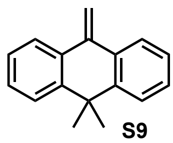


S3, R = H
S4, R = 4-OMe
S5, R = 4-Me

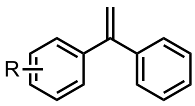
S6, R = 4-F
S7, R = 4-Br



S8

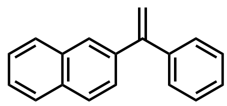


S9

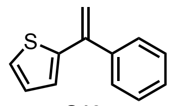


S10, R = 4-Me
S11, R = 4-OH
S12, R = 4-F
S13, R = 4-Cl

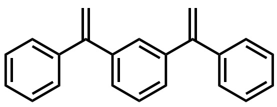
S14, R = 4-Br
S15, R = 4-CF_3
S16, R = 2-Me
S17, R = 3-Me



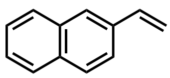
S18



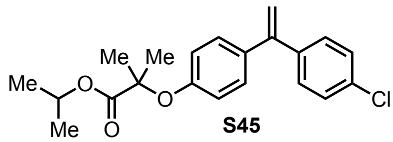
S19



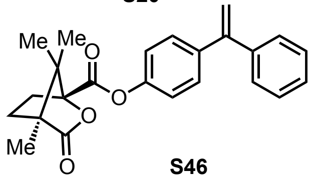
S20



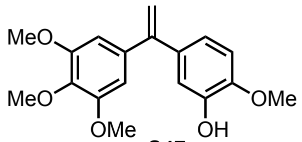
S21



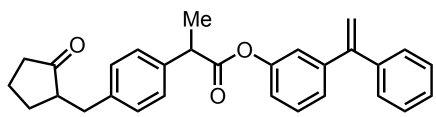
S45



S46

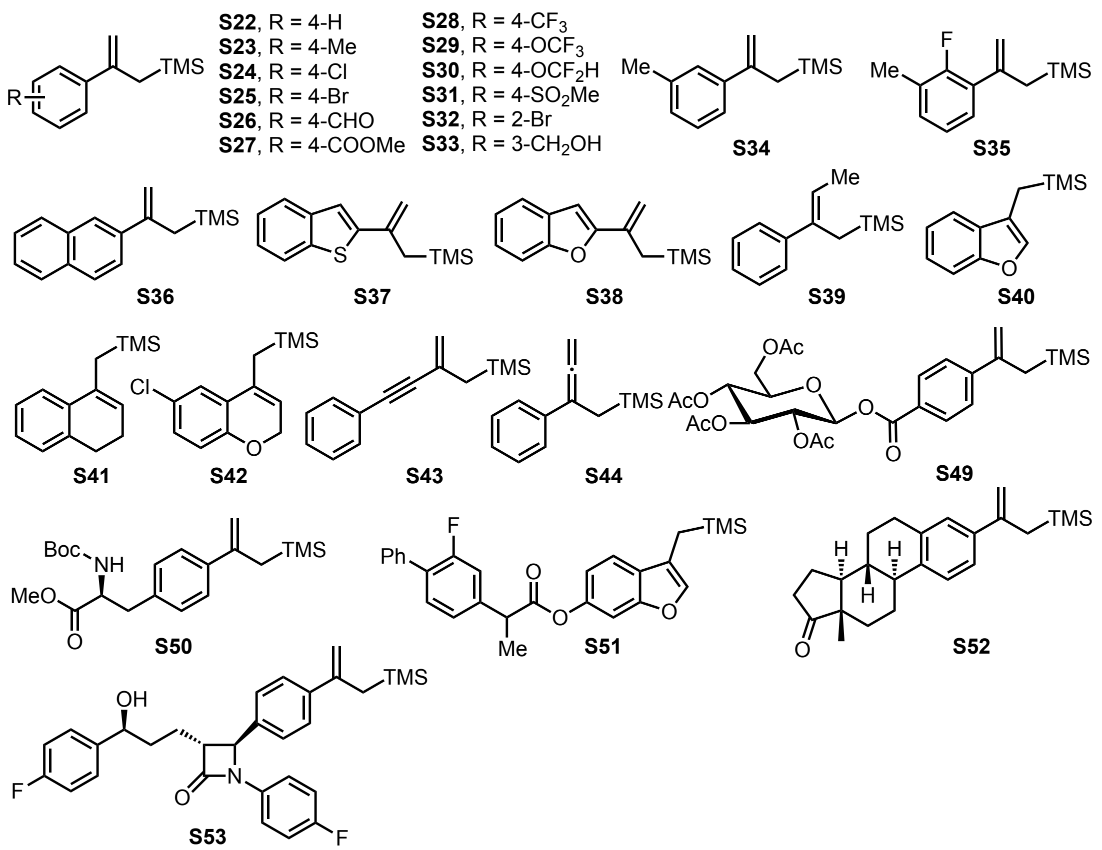


S47

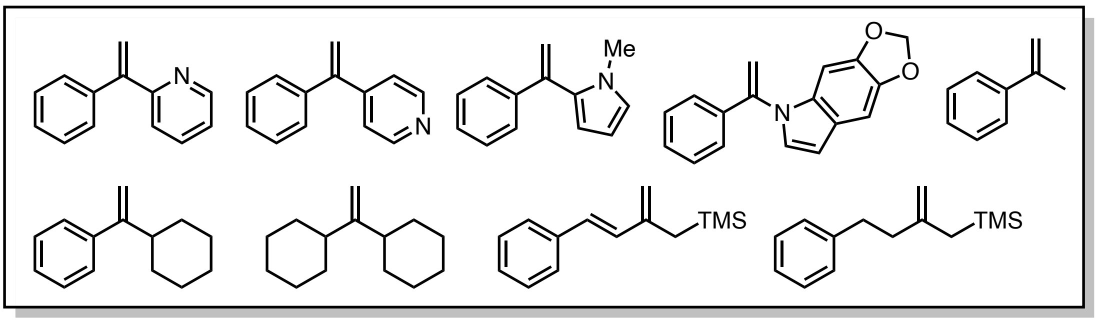


S48

B. Ally(trimethyl) sliane



9. Less reactive substrates



10. DFT calculations

(1) Computation Method

All Density Functional theory (DFT) Calculations were performed using the Gaussian 16 software Package[2] on supercomputer. The geometries of the reactants, transition states, and products were optimized using the M06-2X functional[3] and Grimme's D3 dispersion correction[4] with 6-31G(d) basis set[5]. Vibrational frequency calculations were performed for all the stationary points to confirm each optimized structure is a local minimum or a transition state structure. Single point energy was

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[2] M. J. Frisch, G. W. Trucks, et al. Gaussian 16, Rev. B.01: Wallingford, CT, 2016.

[3] Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215-241.

[4] (a) S. Grimme, J. Antony, S. Ehrlich, H. Krieg, *J. Chem. Phys.* **2010**, *132*, 154104; (b) S. Grimme, S. Ehrlich, L. Goerigk, *J. Comput. Chem.* **2011**, *32*, 1456-1465.

[5] (a) G. A. Petersson, A. Bennett, T. G. Tensfeldt, M. A. Al-Laham, W. A. Shirley, J. Mantzaris, *J. Chem. Phys.* **1988**, *89*, 2193-2198; (b) G. A. Petersson, M. A. Al-Laham, *J. Chem. Phys.* **1991**, *94*, 6081-6090.

calculated using M06-2X functional and Grimme's D3 dispersion correction with 6-311+G(d,p) basis set[6] in SMD continuum solvation model[7] (acetonitrile). Calculation of reaction energy of single electron transfer involving the Ir photoredox catalyst was followed by reference.[8]

(2) Energies and Cartesian Coordinates

1

Thermal correction to Gibbs Free Energy = 0.179721

M06-2X-D3/6-311+G(d,p) SCF energy in solution = -2040.1910286

C	4.38408500	-0.32159900	-0.11734400
C	3.26184200	-1.12397000	-0.01598100
C	4.29202600	1.07347600	-0.26506400
C	2.03881700	-0.46494100	-0.07710800
C	3.06168800	1.69332500	-0.30553000
C	1.88094200	0.93054400	-0.21580900
H	3.32828200	-2.19722500	0.11271700
H	5.18610000	1.68093900	-0.34738200
O	0.40758000	-2.25140300	0.07632600
C	0.31010300	-2.63551400	1.42860600
N	0.74670700	-0.93089400	-0.03383700
N	0.55105800	1.26751500	-0.25567500
H	-0.09233400	-3.64850200	1.39838700
H	-0.32853500	-1.93755200	1.97720800
F	1.54541700	-2.63796200	1.99031500
C	5.75961400	-0.92523700	-0.04806100
F	5.71381100	-2.26255700	-0.00606600
F	6.41881600	-0.50654700	1.04042000
F	6.49648400	-0.57315800	-1.10946900
N	3.02327500	3.15447100	-0.43513200
O	4.06762300	3.71549600	-0.71708900
O	1.95785000	3.70190800	-0.24358600
C	-0.11001800	0.13876200	-0.15164400
C	-1.57677300	0.05419800	-0.13455000
C	-2.27689800	1.23636300	0.15263700
C	-2.28185600	-1.11670600	-0.40726900
C	-3.65991900	1.22398100	0.18058200
H	-1.71903200	2.14705200	0.34320500
C	-3.67613300	-1.10643200	-0.37055500
H	-1.76397300	-2.03268100	-0.66852200

[6] (a) A. D. McLean, G. S. Chandler, *J. Chem. Phys.* **1980**, *72*, 5639-5648. b) R. Krishnan, J. S. Binkley, R. Seeger, J. A.
Pople, *J. Chem. Phys.* **1980**, *72*, 650-654.
[7] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B.* **2009**, *113*, 6378-6396.
[8] W. Zhang, C. A. Morales-Rivera, J. W. Lee, P. Liu, M.-Y. Ngai, *Angew. Chem. Int. Ed.* **2018**, *57*, 9645-9649

C	-4.37458300	0.05199400	-0.07490400
H	-5.45928700	0.05092400	-0.04615100
C	-4.39485900	-2.39269200	-0.67315600
C	-4.43968800	2.47035900	0.50503400
F	-5.14586600	2.30960700	1.63345800
F	-3.64663400	3.53177600	0.66534200
F	-5.31765400	2.75126900	-0.46706200
F	-5.71724700	-2.27633200	-0.52361700
F	-3.97464100	-3.37616300	0.13891100
F	-4.15617900	-2.79815900	-1.92684000

1 radical anion

Thermal correction to Gibbs Free Energy = 0.177134

M06-2X-D3/6-311+G(d,p) SCF energy in solution = -2040.3107425

C	4.42156200	-0.28854800	-0.16198100
C	3.27438500	-1.11851400	-0.17383700
C	4.32853300	1.08806400	-0.17901300
C	2.06484900	-0.46579700	-0.20301000
C	3.07983300	1.73514000	-0.19650700
C	1.88743600	0.95631500	-0.20116500
H	3.34329100	-2.19933200	-0.14009200
H	5.21567900	1.70691700	-0.17232000
O	0.45788500	-2.26141500	-0.03081100
C	0.28005400	-2.52078000	1.33141400
N	0.77597600	-0.94093800	-0.25168000
N	0.57960500	1.28284700	-0.18493000
H	-0.21299000	-3.49467600	1.37225800
H	-0.31493400	-1.72880200	1.79591800
F	1.48402900	-2.59561200	1.96597600
C	5.75335400	-0.95691900	-0.12344200
F	5.90541300	-1.72615400	0.97567100
F	6.77925100	-0.09117900	-0.13479700
F	5.93499300	-1.78972400	-1.17122900
N	3.05653200	3.15643600	-0.19407500
O	4.13744500	3.76285100	-0.19069900
O	1.96677600	3.72405000	-0.19616500
C	-0.11611500	0.13724000	-0.18841500
C	-1.53950400	0.04907500	-0.16716100
C	-2.27501100	1.24990600	0.03625400
C	-2.27661400	-1.15221500	-0.32824400
C	-3.64986200	1.22558900	0.10245800
H	-1.72215800	2.17695700	0.14173600

C	-3.66092700	-1.13919400	-0.25114400
H	-1.76772100	-2.08474000	-0.53551800
C	-4.37981300	0.03273000	-0.02797600
H	-5.46150000	0.02624900	0.04351400
C	-4.42010600	-2.41125100	-0.47834400
C	-4.42632000	2.48715900	0.32711600
F	-5.19765300	2.40190200	1.42950100
F	-3.64815900	3.56533500	0.47235500
F	-5.26912800	2.73923000	-0.69342200
F	-5.50275800	-2.49830600	0.31623800
F	-3.67412100	-3.50576200	-0.24669400
F	-4.87138800	-2.51560700	-1.74152400

·NR^{1}R^2

Thermal correction to Gibbs Free Energy = 0.144978

M06-2X-D3/6-311+G(d,p) SCF energy in solution = -1825.8197212

C	-4.36230700	-0.73631600	-0.00259200
C	-3.22132000	-1.47499400	-0.00872800
C	-4.34886300	0.70514500	0.00479200
C	-1.98310200	-0.76151400	-0.00762200
C	-3.18204300	1.41287400	0.00599300
C	-1.93994100	0.71906000	-0.00007700
H	-3.23259900	-2.55877600	-0.01430000
H	-5.28690700	1.25054700	0.00956900
N	-0.75435800	-1.22647500	-0.01261600
N	-0.67291600	1.11047700	-0.00076000
C	-5.71748200	-1.38894100	-0.00318200
F	-5.62973100	-2.72086500	-0.01042100
F	-6.42411100	-1.01248900	-1.07663300
F	-6.41960500	-1.02389700	1.07712800
N	-3.25418300	2.87978900	0.01357400
O	-4.36491100	3.38103000	0.01841600
O	-2.20392100	3.48391000	0.01440500
C	0.00339800	-0.06682000	-0.00848500
C	1.44466000	-0.11450600	-0.01109600
C	2.18071700	1.08416700	-0.00965600
C	2.10615900	-1.35195900	-0.02172300
C	3.56277300	1.02819500	-0.02048400
H	1.65101300	2.03093600	-0.00581800
C	3.49295000	-1.38236500	-0.03039500
H	1.52292000	-2.26656300	-0.03087200
C	4.22754300	-0.19966300	-0.03278600

H	5.31299300	-0.23110100	-0.05521700
C	4.21778000	-2.70169900	0.00926800
C	4.39281600	2.28442100	-0.00511800
F	5.30173400	2.26693600	-0.98947400
F	3.64373200	3.37926900	-0.15239500
F	5.06675100	2.39804800	1.14717000
F	5.37657400	-2.63821400	-0.65846100
F	3.48230300	-3.68064700	-0.52855400
F	4.50357700	-3.05943100	1.26764500

-NR^{1}R^2

Thermal correction to Gibbs Free Energy = 0.147243

M06-2X-D3/6-311+G(d,p) SCF energy in solution = -1826.0397023

C	-4.40104800	-0.67727000	-0.03739200
C	-3.22053800	-1.41805400	-0.03998200
C	-4.38778600	0.72231300	-0.02264500
C	-2.01097100	-0.73199900	-0.02821500
C	-3.18458200	1.41117900	-0.01130900
C	-1.95507400	0.71371900	-0.01377900
H	-3.24011200	-2.50323100	-0.05818500
H	-5.31137600	1.28648300	-0.02864600
N	-0.73742400	-1.21594200	-0.03471600
N	-0.66385100	1.09679600	-0.01157700
C	-5.71224700	-1.38808900	0.01778900
F	-5.67358300	-2.57935700	-0.60997600
F	-6.70767100	-0.67898700	-0.54681400
F	-6.11318600	-1.64953800	1.28042900
N	-3.24566800	2.86690100	-0.00490400
O	-4.35229400	3.39979800	-0.02254500
O	-2.19925700	3.48688700	0.01936700
C	-0.01417000	-0.09163100	-0.02372800
C	1.45586400	-0.13074300	-0.02306700
C	2.19443100	1.05537300	-0.02361300
C	2.13207800	-1.35511800	-0.03199000
C	3.58514200	1.00902900	-0.03275600
H	1.65559100	1.99820600	-0.02623600
C	3.52105600	-1.38315200	-0.04144000
H	1.54626900	-2.26860400	-0.04113000
C	4.26383000	-0.20487800	-0.04215800
H	5.34742800	-0.23371700	-0.06550600
C	4.24360600	-2.69615900	0.00219600
C	4.36205100	2.29143400	0.01354900

F	5.61842900	2.13595800	-0.44373000
F	3.78839900	3.25540100	-0.71953900
F	4.46763900	2.76998900	1.26564900
F	5.41987600	-2.64239200	-0.64990000
F	3.52957800	-3.68933500	-0.54574800
F	4.52755900	-3.07314400	1.26237900

$\cdot OCH_2F$

Thermal correction to Gibbs Free Energy = 0.006082

M06-2X-D3/6-311+G(d,p) SCF energy in solution = -214.2919238

C	0.00000000	0.44725700	0.00000000
H	0.08537700	1.08810000	0.89716900
H	0.08537700	1.08810000	-0.89716900
O	-1.19957500	-0.11805800	0.00000000
F	1.04731600	-0.43503100	0.00000000

$^{-}OCH_2F$

Thermal correction to Gibbs Free Energy = 0.006078

M06-2X-D3/6-311+G(d,p) SCF energy in solution = -214.4721602

C	0.00000000	0.47610600	0.00000000
H	0.38866800	1.04157000	0.90676200
H	0.38866800	1.04157000	-0.90676200
O	-1.21618800	0.13030900	0.00000000
F	0.99468500	-0.66469400	0.00000000

11. Crystallographic data

Crystal growth for compound 1: In a 5 mL vial, about 5 mg of the respective compound was dissolved in DCM (2 mL). The vial was left uncovered and placed in a 20 mL vial with hexane (8 mL). The 20 mL vial was sealed and stored at room temperature for crystal growth. After slow exchange of DCM and hexane, crystals (suitable for X-ray analysis) are appeared on the bottom of the inner vial.

X-ray data for the compound was collected at room temperature on a XtaLAB Synergy-DS instrument with a Cu microsource (λ = 1.54184 Å) and a hybrid photon counting detector. The structures were solved with the SHELXT solution program by using Olex 2[9] as the graphical interface. The model was refined using Least Squares minimisation with the 2018/3 version of the program SHELXL.[10]

[9] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst*. **2009**, *42*, 339-341.
[10] G. M. Sheldrick, SHELXTL; Siemens analytical X-ray systems: madison, Wisconsin, USA.

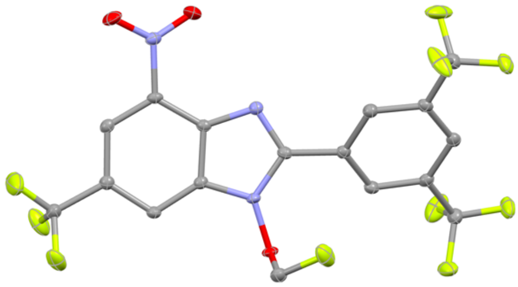
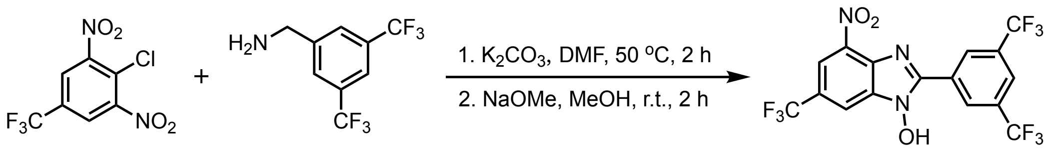


Figure S13. X-ray crystal structure of **1** (ellipsoids set at 50% probability)

Identification code	CCDC 2387216
Empirical formula	$C_{17}H_7F_{10}N_3O_3$
Formula weight	491.26
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	7.29637(7)
b/Å	8.22828(7)
c/Å	29.4798(2)
α/°	90
β/°	94.8307(8)
γ/°	90
Volume/Å^3	1763.58(3)
Z	4
ρ_{calc}g/cm^3	1.850
μ/mm^{-1}	1.802
F(000)	976.0
Crystal size/mm^3	0.11 × 0.08 × 0.07
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	6.018 to 154.502
Index ranges	$-8 \leq h \leq 9$, $-10 \leq k \leq 3$, $-36 \leq l \leq 35$
Reflections collected	12242
Independent reflections	3596 [R_{int} = 0.0215, R_{sigma} = 0.0186]
Data/restraints/parameters	3596/126/353
Goodness-of-fit on F^2	1.051
Final R indexes [I>=2σ (I)]	R_1 = 0.0374, wR_2 = 0.0959
Final R indexes [all data]	R_1 = 0.0389, wR_2 = 0.0973
Largest diff. peak/hole / e Å^{-3}	0.49/-0.25

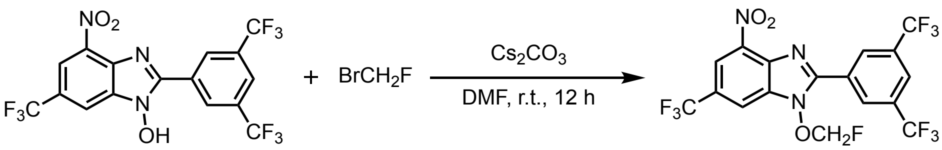
12. Synthesis of substrates and characterization data

2-(3,5-Bis(trifluoromethyl)phenyl)-4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-ol (S1).



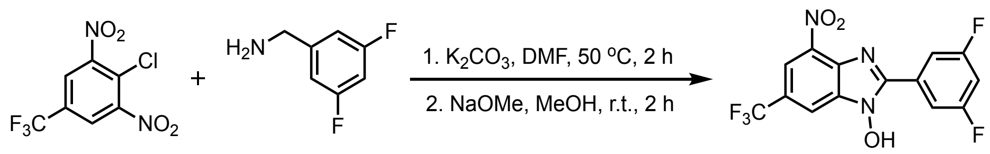
To a round bottom flask equipped with a magnetic stir bar, 2-chloro-1,3-dinitro-5-(trifluoromethyl)benzene (50.0 mmol, 1.0 equiv.), and (3,5-bis (trifluoromethyl)phenyl)methanamine (60.0 mmol, 1.2 equiv.) was added DMF. After the reaction mixture was stirred for 10 min, K_2CO_3 (30.0 mmol, 0.6 equiv.) was added. The resulting mixture was heated at 50 °C for 2 h and then cooled to room temperature and quenched with 1 M HCl aqueous solution. The mixture was transferred to a 250 mL separatory funnel and extracted with ethyl acetate. The combined organic layers were sequentially washed with 1 M HCl aqueous solution, water, and brine. The organic layer was then dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was dissolved in dry methanol under argon atmosphere followed by the addition of NaOMe (100.0 mmol, 2.0 equiv.). The reaction mixture was stirred under argon at room temperature for 2 h and then poured into 100 mL of 1 M HCl aqueous solution. The aqueous layer was transferred to a separatory funnel and extracted with ethyl acetate. The combined organic layers were sequentially washed with 1 M HCl aqueous solution, water, and brine. The organic layer was collected, dried with anhydrous Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the resulting residue was sonicated with dichloromethane and solid was collected by filtration to afford the desired product **S1** as a yellow solid (12.9 g, 56 % yield). **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.85 (s, 2H), 8.43 (s, 2H), 8.38 (s, 1H) ppm.

(3,5-Bis(trifluoromethyl)phenyl)-1-(fluoromethoxy)-4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (1).



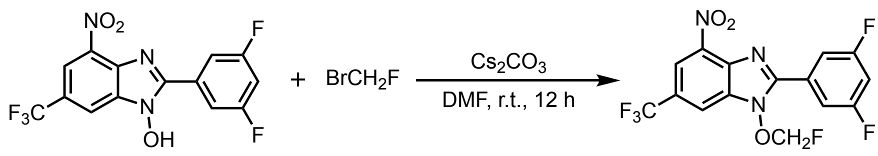
An oven dried 100 mL round bottom flask was charged with a stirring bar, 2-(3,5-bis(trifluoromethyl)phenyl)-4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*] imidazol-1-ol **S1** (12.9 g, 28.1 mmol, 1.0 equiv.), Cs_2CO_3 (33.6 mmol, 1.2 equiv.) and anhydrous DMF (50 mL) was added. To this suspension, fluorobromomethane (42.0 mmol, 1.5 equiv.) was added and the reaction mixture was stirred overnight at room temperature. After quenching with H_2O (100 mL) the reaction mixture was extracted three times with EtOAc. The separated organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The resulting crude product was purified by column chromatography (hexane: EtOAc = 30: 1) to give the product **1** as a yellow solid (10.2 g, 75% yield, m.p.: 202 – 204 °C). **^{1}H NMR (400 MHz, DMSO-d_6):** δ 8.71 (s, 2H), 8.64 (s, 1H), 8.49-8.45 (m, 2H), 6.10 (d, J = 52.0 Hz, 2H) ppm; **^{13}C NMR (151 MHz, DMSO-d_6):** δ 149.7, 138.7, 134.0, 132.8, 131.0 (q, J = 33.7 Hz), 129.5 (d, J = 4.2 Hz), 129.0, 125.4, 124.3 (q, J = 33.7 Hz), 123.3 (q, J = 272.9 Hz), 122.9 (q, J = 273.2 Hz), 117.0 (q, J = 3.6 Hz), 114.2 (d, J = 2.7 Hz), 108.2 (d, J = 232.8 Hz) ppm; **^{19}F NMR (376 MHz, DMSO-d_6):** δ -59.7 (s, 3F), -61.6 (s, 6F), -150.1 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{17}H_7F_{10}N_3NaO_3$ $[M+Na]^+$: 514.0220; found: 514.0217.

2-(3,5-Difluorophenyl)-4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-ol (S1a).



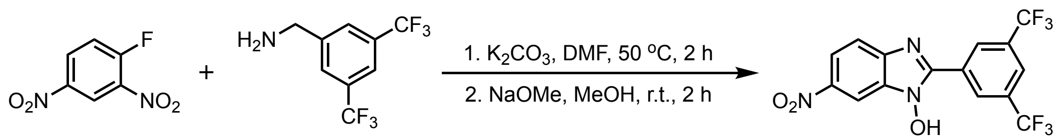
To a round bottom flask equipped with a magnetic stir bar, 2-chloro-1,3-dinitro-5-(trifluoromethyl)benzene (4.0 mmol, 1.0 equiv.), and (3,5- difluorophenyl) methanamine (4.8 mmol, 1.2 equiv.) was added DMF. After the reaction mixture was stirred for 10 min, K_2CO_3 (2.4 mmol, 0.6 equiv.) was added. The resulting mixture was heated at 50 °C for 2 h and then cooled to room temperature and quenched with 1 M HCl aqueous solution. The mixture was transferred to a 250 mL separatory funnel and extracted with ethyl acetate. The combined organic layers were sequentially washed with 1 M HCl aqueous solution, water, and brine. The organic layer was then dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was dissolved in dry methanol under argon atmosphere followed by the addition of NaOMe (8.0 mmol, 2.0 equiv.). The reaction mixture was stirred under argon at room temperature for 2 h and then poured into 50 mL of 1 M HCl aqueous solution. The aqueous layer was transferred to a 250 mL separatory funnel and extracted with ethyl acetate. The combined organic layers were sequentially washed with 1 M HCl aqueous solution, water, and brine. The organic layer was collected, dried with anhydrous Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the resulting residue was sonicated with dichloromethane and solid was collected by filtration to afford the desired product S1 as a yellow solid (890.4 mg, 62 % yield over 2 steps). **^{1}H NMR (400 MHz, DMSO-d$_6$):** δ 8.45 - 8.44 (m, 1H), 8.38 - 8.37 (m, 1H), 8.02 - 7.96 (m, 2H), 7.64 - 7.58 (m, 1H) ppm.

2-(3,5-Difluorophenyl)-1-(fluoromethoxy)-4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*]imidazole (1a).



An oven dried 100 ml round bottom flask was charged with a stirring bar, 2-(3,5-difluorophenyl)-4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*]imidazol-1-ol **S1a** (2.4 mmol, 1.0 equiv.), Cs_2CO_3 (2.9 mmol, 1.2 equiv.) and anhydrous DMF was added. To this suspension, fluorobromomethane (3.6 mmol, 1.5 equiv.) was added and the reaction mixture was stirred overnight at room temperature. After quenching with water the reaction mixture was extracted three times with EtOAc. The separated organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The resulting crude product was purified by column chromatography (hexane: EtOAc = 30: 1) to give the product **1a** as a white solid (703.9 mg, 75 % yield, m.p.: 189 - 190°C). **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.54 (s, 1H), 8.39 (s, 1H), 7.85 - 7.79 (m, 2H), 7.63-7.57 (m, 1H), 6.10 (d, *J* = 52.0 Hz, 2H) ppm; **^{13}C NMR (151 MHz, DMSO-*d*$_6$):** δ 162.3 (dd, *J* = 247.5 Hz, 13.3 Hz), 149.9 (t, *J* = 3.5 Hz), 138.5, 134.2, 132.8, 129.3 (t, *J* = 10.7 Hz), 124.1 (q, *J* = 33.8 Hz), 123.3 (q, *J* = 272.7 Hz), 116.8 (q, *J* = 3.6 Hz), 114.0 (t, *J* = 3.5 Hz), 112.3 (dd, *J* = 22.2 Hz, 6.5 Hz), 108.1 (d, *J* = 233.3 Hz), 107.6 (t, *J* = 25.8 Hz) ppm; **^{19}F NMR (376 MHz, DMSO-*d*$_6$):** δ -59.8 (s, 3F), -107.9 (s, 2F), -150.0 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{15}H_7F_6N_3NaO_3$ $[M+Na]^+$: 414.0284; found: 414.0273.

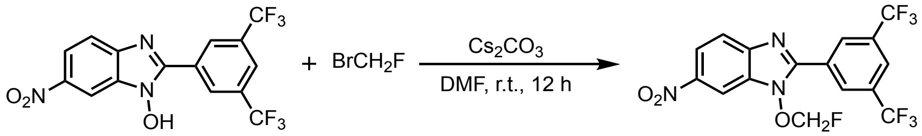
2-(3,5-Bis(trifluoromethyl)phenyl)-6-nitro-1*H*-benzo[*d*]imidazol-1-ol (S1b).



To a round bottom flask equipped with a magnetic stir bar, 1-fluoro-2,4-dinitrobenzene (4.0 mmol, 1.0 equiv.), and (3,5-bis(trifluoromethyl)phenyl) methanamine (4.8 mmol, 1.2 equiv.) was added DMF. After the reaction mixture was stirred for 10 min, K_2CO_3 (2.4 mmol, 0.6 equiv.) was added. The resulting mixture was heated at 50 °C for 2 h and then cooled to room temperature and quenched with 1 M HCl aqueous solution. The mixture was transferred to a 250 mL separatory funnel and extracted with ethyl acetate. The combined organic layers were sequentially washed with 1 M HCl aqueous solution, water, and brine. The organic layer was then dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting residue was dissolved in dry methanol under argon atmosphere followed by the addition of NaOMe (8.0 mmol, 2.0 equiv.). The reaction mixture was stirred under argon at room temperature for 2 h and then poured into 50 mL of 1 M HCl aqueous solution. The aqueous layer was transferred to a 250 mL separatory funnel and extracted with ethyl acetate. The combined organic layers were sequentially washed with 1 M

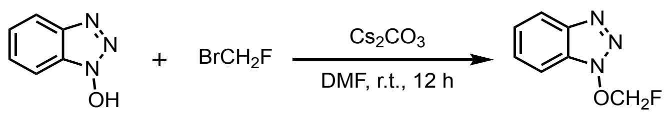
HCl aqueous solution, water, and brine. The organic layer was collected, dried with anhydrous Na_2SO_4, and filtered. The filtrate was concentrated *in vacuo* and the resulting residue was sonicated with dichloromethane and solid was collected by filtration to afford the desired product **S1b** as a yellow solid (938.5 mg, 60 % yield over 2 steps). **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.78 - 8.77 (m, 2H), 8.30 - 8.28 (m, 2H), 8.05 - 8.02 (m, 1H), 7.79 - 7.77 (m, 1H) ppm.

2-(3,5-Bis(trifluoromethyl)phenyl)-1-(fluoromethoxy)-6-nitro-1*H*-benzo[*d*]imidazole (1b).



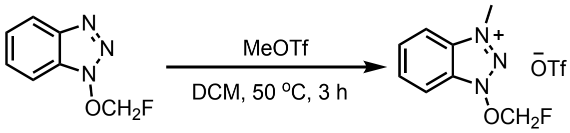
An oven dried 100 ml round bottom flask was charged with a stirring bar, 2-(3,5-Bis(trifluoromethyl)phenyl)-6-nitro-1*H*-benzo[*d*]imidazol-1-ol **S1b** (2.4 mmol, 1.0 equiv.), Cs_2CO_3 (2.88 mmol, 1.2 equiv.) and anhydrous DMF was added. To this suspension, fluorobromomethane (3.6 mmol, 1.5 equiv.) was added and the reaction mixture was stirred overnight at room temperature. After quenching with water the reaction mixture was extracted three times with EtOAc. The separated organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The resulting crude product was purified by column chromatography (hexane: EtOAc = 30: 1) to give the product **1b** as a white solid (660.0 mg, 65 % yield, m.p.: 204 - 206°C). **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.68 (s, 2H), 8.61 - 8.60 (m, 1H), 8.41 (s, 1H), 8.21 (dd, J = 9.2 Hz, 2.4Hz, 1H), 7.99-7.97 (m, 1H), 6.11 (d, J = 52.0 Hz, 2H) ppm; **^{13}C NMR (151 MHz, DMSO-*d*$_6$):** δ 148.7, 144.2, 141.7, 130.9 (q, J = 33.5 Hz), 130.9, 129.5, 129.2, 124.9, 123.0 (q, J = 273.5 Hz), 121.0, 119.0, 108.1 (d, J = 232.1 Hz), 106.9 ppm; **^{19}F NMR (376 MHz, DMSO-*d*$_6$):** δ -61.6 (s, 6F), -150.1 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{16}H_8F_7N_3NaO_3$ $[M+Na]^+$: 446.0346; found: 446.0341.

1-(Fluoromethoxy)-1*H*-benzo[*d*][1,2,3]triazole (S1c).



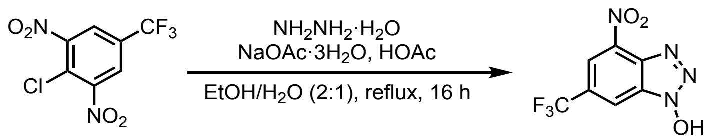
An oven dried 100 ml round bottom flask was charged with a stirring bar, *N*-hydroxybenzotriazole (5 mmol, 1.0 equiv.), Cs_2CO_3 (6.0 mmol, 1.2 equiv.) and anhydrous DMF was added. To this suspension, fluorobromomethane (7.5 mmol, 1.5 equiv.) was added and the reaction mixture was stirred overnight at room temperature. After quenching with water the reaction mixture was extracted three times with EtOAc. The separated organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The resulting crude product was purified by column chromatography (hexane: EtOAc = 20: 1) to give the product **S1c** as a white solid (768.4 mg, 92 % yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.03-8.00 (m, 1H), 7.65-7.62 (m, 1H), 7.57-7.53 (m, 1H), 7.43-7.39 (m, 1H), 5.98 (d, J = 52.8 Hz, 2H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 143.6, 128.9, 128.7, 125.2, 120.3, 109.2 (d, J = 2.2 Hz), 106.9 (d, J = 238.0 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -149.3 ppm; **HRMS** (m/z) (ESI): calcd. for $C_7H_6FN_3NaO$ $[M+Na]^+$: 190.0387; found: 190.0387.

1-(Fluoromethoxy)-3-methyl-1*H*-benzo[*d*][1,2,3]triazol-3-ium trifluoromethanesulfonate (1c).



To a solution of 1-(fluoromethoxy)-1*H*-benzo[*d*][1,2,3]triazole **S1c** (5 mmol, 1.0 equiv.) in dry DCM (20 mL) under argon atmosphere was added methyl trifluoromethanesulfonate (10 mmol, 2.0 equiv.). The reaction was stirred at 50 ºC for 3 h, and then cooled to room temperature. The precipitated solid was filtered, washed with Et_2O and dried under vacuum to afford *N*-fluoromethoxybenzotriazolium salts **1c** as a white solid (1.5 g, 90 % yield, m.p.: 129 - 130ºC). **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.48 - 8.43 (m, 1H), 8.30 - 8.26 (m, 1H), 8.13 - 8.08 (m, 1H), 6.35 (d, J = 50.8 Hz, 2H), 4.66 (s, 3H) ppm; **^{13}C NMR (151 MHz, DMSO-*d*$_6$):** δ 135.3, 132.7, 132.0, 129.9, 120.7 (q, J = 322.4 Hz), 114.4, 112.2, 108.6 (d, J = 240.0 Hz), 38.5 ppm; **^{19}F NMR (376 MHz, DMSO-*d*$_6$):** δ -77.8 (s, 3F), -147.8 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_9H_{10}F_4N_3O_4S$ $[M+H]^+$: 332.0323; found: 332.0312.

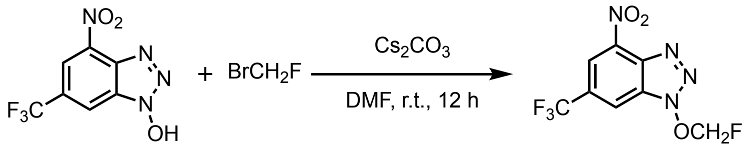
4-Nitro-6-(trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazol-1-ol (S1da).



To a round bottom flask equipped with a stir bar, 1,3-dinitro-2-chloro -5-trifluoromethylbenzene (10 mmol, 1.0 equiv.), $NaOAc\cdot 3H_2O$ (50 mmol, 5.0 equiv.) and HOAc (50 mmol, 5.0 equiv.) was added successively, then EtOH and H_2O (v/v = 2:1) were added. After the reaction mixture was stirred for 10 min, $NH_2NH_2\cdot H_2O$ (40 mmol, 4.0 equiv.) was added. The resulting mixture was then refluxed at 105 ºC for 16 h. After cooling to room temperature, the solution was concentrated in vacuo, quenched with 1 M HCl aqueous solution and extracted with EtOAc. The combined organic layers were then dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting crude product was further washed with DCM to afford the target S1da as a white solid (1.61 g, 65% yield). **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.79 - 8.78

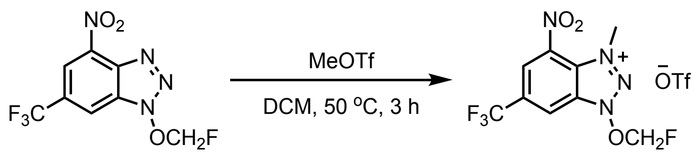
(m, 1H), 8.54 - 8.53 (m, 1H) ppm;

1-(Fluoromethoxy)-4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazole (S1db).



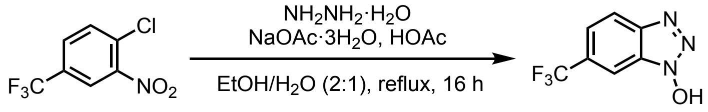
An oven dried 100 ml round bottom flask was charged with a stirring bar, 4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazole-1-ol (1 mmol, 1.0 equiv.), Cs_2CO_3 (1.2 equiv.) and anhydrous DMF was added. To this suspension, fluorobromomethane (1.5 equiv.) was added and the reaction mixture was stirred overnight at room temperature. After quenching with water the reaction mixture was extracted three times with EtOAc. The separated organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The resulting crude product was purified by column chromatography (hexane: EtOAc = 30: 1) to give the product **S1db** as a white solid (238.0 mg, 85 % yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.52 - 8.51 (m, 1H), 8.35 (s, 1H), 6.12 (d, *J* = 52.0 Hz, 2H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 139.2, 137.0, 131.1 (q, *J* = 35.1 Hz), 130.9, 122.4 (q, *J* = 274.6 Hz), 119.4 (q, *J* = 3.1 Hz), 114.4 - 114.3 (m), 107.4 (d, *J* = 240.5 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -62.1 (s, 3F), -149.5 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_8H_4F_4N_4NaO_3$ $[M+Na]^+$: 303.0112; found: 303.0114.

1-(Fluoromethoxy)-3-methyl-4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazol-3-ium trifluoromethanesulfonate (1d).



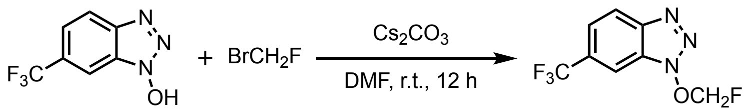
To a solution of 1-(fluoromethoxy)-4-nitro-6-(trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazole **S1db** (1 mmol, 1.0 equiv.) in dry DCM (20 mL) under argon atmosphere, was added methyl trifluoromethanesulfonate (2.0 mmol, 2.0 equiv.). The reaction was stirred at 50 ºC for 3 h and then cooled to room temperature. The precipitated solid was washed with Et_2O and dried under vacuum to affording *N*-fluoromethoxybenzotriazolium salts **1d** as a yellow solid (364.1 mg, 82 % yield, m.p.: 189 - 191ºC). **^{1}H NMR (400 MHz, DMSO-d_6):** δ 9.57 - 9.56 (m, 1H), 9.14 - 9.13 (m, 1H), 6.42 (d, *J* = 50.4 Hz, 2H), 4.83 (s, 3H) ppm; **^{13}C NMR (151 MHz, DMSO-d_6):** δ 137.4, 132.6, 131.3 (q, *J* = 35.5 Hz), 129.2, 126.0 (q, *J* = 3.0 Hz), 121.8 (q, *J* = 274.4 Hz), 120.6 (q, *J* = 322.4 Hz), 118.8 (q, *J* = 4.4 Hz), 108.9 (d, *J* = 243.0 Hz), 44.6 ppm; **^{19}F NMR (376 MHz, DMSO-d_6):** δ -61.0 (s, 3F), -77.9 (s, 3F), -147.6 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{10}H_7F_7N_4NaO_6S$ $[M+Na]^+$: 466.9867; found: 466.9861.

6-(Trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazol-1-ol (S1ea).



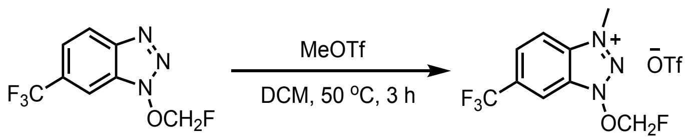
To a round bottom flask equipped with a stir bar, 1-chloro-2-nitro -4-(trifluoromethyl)benzene (10 mmol, 1.0 equiv.), $NaOAc \cdot 3H_2O$ (50 mmol, 5.0 equiv.) and HOAc (50 mmol, 5.0 equiv.) was added successively, then EtOH and H_2O (v/v = 2:1) were added. After the reaction mixture was stirred for 10 min, $NH_2NH_2 \cdot H_2O$ (40 mmol, 4.0 equiv.) was added. The resulting mixture was then refluxed at 105 ºC for 16 h. After cooling to room temperature, the solution was concentrated in vacuo, quenched with 1 M HCl aqueous solution and extracted with EtOAc. The combined organic layers were then dried with anhydrous Na_2SO_4, filtered, and concentrated in vacuo. The resulting crude product was further washed with DCM to afford the target **S1ea** as a white solid (1.32 g, 65% yield). **^{1}H NMR (400 MHz, DMSO-d$_6$):** δ 8.25 - 8.23 (m, 1H), 8.19 (s, 1H), 7.71-7.68 (m, 1H) ppm;

1-(Fluoromethoxy)-6-(trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazole (S1eb).



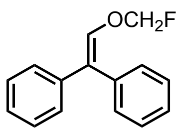
An oven dried 100 ml round bottom flask was charged with a stirring bar, 6-(trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazol-1-ol **S1ea** (1 mmol, 1.0 equiv.), Cs_2CO_3 (1.2 mmol, 1.2 equiv.) and anhydrous DMF was added. To this suspension, fluorobromomethane (1.5 mmol, 1.5 equiv.) was added and the reaction mixture was stirred overnight at room temperature. After quenching with water, the reaction mixture was extracted three times with EtOAc. The separated organic layers were dried over anhydrous Na_2SO_4, filtered and evaporated to dryness. The resulting crude product was purified by column chromatography (hexane: EtOAc = 30: 1) to give the product **S1eb** as a white solid (176.3 mg, 75 % yield). **^{1}H NMR (400 MHz, DMSO-*d$_6$*):** δ 8.36-8.33 (m, 1H), 8.29 - 8.28 (m, 1H), 7.78 (dd, J = 8.8 Hz, 1.6 Hz, 1H), 6.22 (d, J = 52.0 Hz, 2H) ppm; **^{13}C NMR (151 MHz, DMSO-*d$_6$*):** δ 144.0, 129.2 (q, J = 32.3 Hz), 127.1, 123.8 (q, J = 273.0 Hz), 121.63 (q, J = 3.2 Hz), 121.56, 108.3 (q, J = 5.0 Hz), 107.8 (d, J = 233.7 Hz) ppm; **^{19}F NMR (376 MHz, DMSO-*d$_6$*):** δ -60.6 (s, 3F), -149.7 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_8H_6F_4N_3O$ $[M+H]^+$: 236.0442; found: 236.0450.

1-(Fluoromethoxy)-3-methyl-6-(trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazol-3-ium trifluoromethanesulfonate (1e).



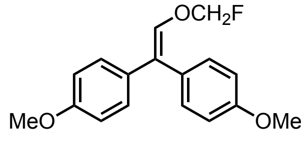
To a solution of 1-(fluoromethoxy)-6-(trifluoromethyl)-1*H*-benzo[*d*][1,2,3]triazole **S1eb** (1 mmol, 1.0 equiv.) in dry DCM (20 mL) under argon atmosphere, was added methyl trifluoromethanesulfonate (MeOTf, 2.0 mmol, 2.0 equiv.). The reaction was stirred at 50 ºC for 3 h, and then cooled to room temperature. The precipitated solid was washed with Et_2O and dried under vacuum to afford *N*-fluoromethoxybenzotriazolium salts **1e** as a yellow solid (287.3 mg, 72 % yield, m.p.: 169 - 170ºC). **^{1}H NMR (400 MHz, DMSO-*d*$_6$):** δ 8.99 (s, 1H), 8.75-8.72 (m, 1H), 8.58 - 8.45 (m, 1H), 6.37 (d, *J* = 50.8 Hz, 2H), 4.74 (s, 3H) ppm; **^{13}C NMR (151 MHz, DMSO-*d*$_6$):** δ 136.9, 132.2 (q, *J* = 33.7 Hz), 129.7, 128.1 (q, *J* = 2.4 Hz), 123.0 (q, *J* = 273.8 Hz), 120.6 (q, *J* = 322.4 Hz), 116.8, 111.8 (q, *J* = 4.7 Hz), 108.7 (d, *J* = 241.0 Hz), 39.0 ppm; **^{19}F NMR (376 MHz, DMSO-*d*$_6$):** δ -61.0 (s, 3F), -77.9 (s, 3F), -147.9 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{10}H_9F_7N_3O_4S$ $[M+H]^+$: 400.0197; found: 400.0198.

(2-(Fluoromethoxy)ethene-1,1-diyl)dibenzene (3).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (31.0 mg, 68% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.38 - 7.21 (m, 10H), 6.68 (s, 1H), 5.49 (d, *J* = 54.4 Hz, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.3, 139.5, 136.9, 130.2, 128.5, 128.3, 128.2, 127.4, 127.3, 125.1, 102.6 (d, *J* = 222.3 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -150.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{15}H_{13}FNaO$ $[M+Na]^+$: 251.0843; found: 251.0836.

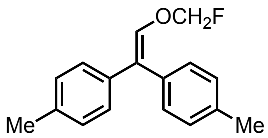
4,4'-(2-(Fluoromethoxy)ethene-1,1-diyl)bis(methoxybenzene) (4).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (32.3 mg, 56% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.34 -7.32 (m, 2H), 7.18 - 7.16 (m, 2H), 6.91 - 6.85 (m, 4H), 6.58 (s, 1H), 5.50 (d, *J* = 54.8 Hz, 2H), 3.83 (s, 3H), 3.82 (s, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 159.0, 158.7, 139.8, 132.2, 131.3, 129.54, 129.49, 124.3, 113.9, 113.5, 102.7 (d, *J* = 221.7 Hz), 55.4, 55.3 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -149.8

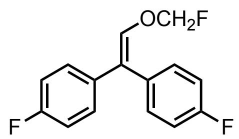
ppm; **HRMS** (m/z) (ESI): calcd. for $C_{17}H_{18}FO_3$ [M+H]$^+$: 289.1234; found: 289.1229.

4,4'-(2-(Fluoromethoxy)ethene-1,1-diyl)bis(methylbenzene) (5).



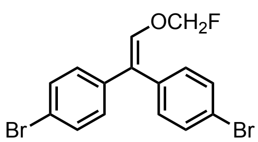
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (23.6 mg, 46% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.41 (d, *J* = 8.0 Hz, 2H), 7.31 - 7.24 (m, 6H), 6.78 (s, 1H), 5.62 (d, *J* = 54.8 Hz, 2H), 2.50 (s, 3H), 2.49 (s, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 140.5, 137.04, 136.98, 136.7, 134.1, 130.0, 129.2, 128.9, 128.2, 124.9, 102.6 (d, *J* = 221.9 Hz), 21.4, 21.2 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -149.9 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{17}H_{18}FO$ [M+H]$^+$: 257.1336; found: 257.1332.

4,4'-(2-(Fluoromethoxy)ethene-1,1-diyl)bis(fluorobenzene) (6).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (25.4 mg, 48% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.35 - 7.32 (m, 2H), 7.20 - 7.16 (m, 2H), 7.06 - 6.99 (m, 4H), 6.62 (s, 1H), 5.51 (d, *J* = 54.4 Hz, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 163.4 (d, *J* = 38.4 Hz), 161.0 (d, *J* = 38.7 Hz), 141.1, 135.3 (d, *J* = 3.3 Hz), 132.7 (d, *J* = 3.5 Hz), 131.7 (d, *J* = 8.0 Hz), 130.0 (d, *J* = 8.0 Hz), 123.2, 115.5 (d, *J* = 21.5 Hz), 115.2 (d, *J* = 21.4 Hz), 102.6 (d, *J* = 222.7 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -114.4 (s, 1F), -115.1 (s, 1F), -150.0 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{15}H_{12}F_3O$ [M+H]$^+$: 265.0835; found: 265.0828.

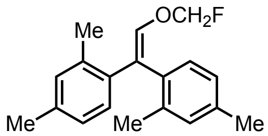
4,4'-(2-(Fluoromethoxy)ethene-1,1-diyl)bis(bromobenzene) (7).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (30.7 mg, 40% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.43 (d, *J* = 8.4 Hz, 2H), 7.22 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.67 (s, 1H), 5.51 (d, *J* = 54.0 Hz, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.8, 137.9, 135.3, 131.8, 131.7, 131.5, 129.9, 123.1, 121.6, 121.5, 102.5 (d, *J* = 223.4 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -150.0 ppm;

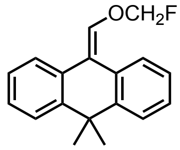
HRMS (m/z) (ESI): calcd. for $C_{15}H_{11}Br_2FNaO$ $[M+Na]^+$: 408.9033; found: 408.9034.

4,4'-(2-(Fluoromethoxy)ethene-1,1-diyl)bis(1,3-dimethylbenzene) (8).



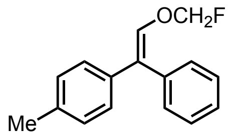
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (25.6 mg, 45% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.13 - 7.11 (m, 1H), 7.05 (s, 1H), 7.02 - 6.94 (m, 4H), 6.49 (s, 1H), 5.47 (d, J = 54.8 Hz, 2H), 2.33 (s, 6H), 2.25 (s, 3H), 2.10 (s, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 142.0, 137.0, 136.9, 136.8, 136.6, 136.0, 133.8, 131.7, 131.1, 130.6, 130.1, 126.5, 126.3, 123.6, 102.4 (d, J = 221.7 Hz), 21.3, 21.1, 20.6, 20.4 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -149.6 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{19}H_{21}FNaO$ $[M+Na]^+$: 307.1469; found: 307.1458.

10-((Fluoromethoxy)methylene)-9,9-dimethyl-9,10-dihydroanthracene (9).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (22.5 mg, 42% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.96 - 7.94 (m, 1H), 7.56 - 7.52 (m, 2H), 7.45 - 7.43 (m, 1H), 7.30 - 7.20 (m, 4H), 6.95 (s, 1H), 5.58 (d, J = 54.8 Hz, 2H), 1.59 (s, 6H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 144.9, 144.2, 140.2, 134.6, 132.1, 128.4, 127.4, 127.1, 126.4, 125.7, 123.7, 123.6, 123.3, 119.2, 102.8 (d, J = 222.8 Hz), 39.8, 29.0 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -149.9 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{18}H_{18}FO$ $[M+H]^+$: 269.1336; found: 269.1329.

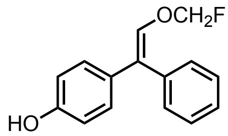
1-(2-(Fluoromethoxy)-1-phenylvinyl)-4-methylbenzene (10).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (19.9 mg, 41% yield, 1.1:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.53 - 7.30 (m, 9H), 6.80 (s, 1H), 5.63 (dd, J = 54.8 Hz, 2.4 Hz, 2H), 2.50 (d, J = 6.0 Hz, 3H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.0, 139.7, 137.1, 136.6, 130.1, 129.2, 128.5, 128.2, 127.3, 125.1, 102.6 (d, J = 222.1 Hz), 21.4 ppm; **^{19}F NMR (376 MHz,**

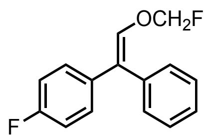
$CDCl_3$): δ -150.0 ppm; **Data of the other isomer: ^{13}C NMR (101 MHz, $CDCl_3$):** δ 140.8, 137.1, 137.0, 133.9, 130.0, 128.9, 128.3, 128.1, 127.2, 125.0, 102.6 (d, J = 222.1 Hz), 21.2 ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -150.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{16}H_{15}FNaO$ $[M+Na]^+$: 265.0999; found: 265.0988.

4-(2-(Fluoromethoxy)-1-phenylvinyl)phenol (11).



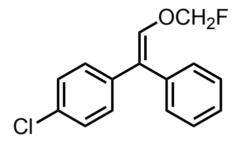
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate= 80: 1). Yellow oil (28.3 mg, 58% yield, 1.2:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.28 - 7.14 (m, 6H), 7.02 - 7.00 (m, 1H), 6.73 - 6.67 (m, 2H), 6.53 (s, 1H), 5.41 (dd, J = 54.8 Hz, 6.0 Hz, 2H), 5.26 (s, 1H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, $CDCl_3$):** δ 154.9, 140.7, 139.7, 132.1, 131.5, 130.1, 128.5, 127.3, 124.6, 115.4, 102.7 (d, J = 222.0 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -149.7 ppm; **Data of the other isomer: ^{13}C NMR (101 MHz, $CDCl_3$):** δ 154.7, 140.3, 137.1, 129.7, 129.4, 128.4, 128.1, 127.3, 124.6, 115.1, 102.6(d, J = 221.9 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -149.8 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{15}H_{13}FNaO_2$ $[M+Na]^+$: 267.0792; found: 267.0798.

1-Fluoro-4-(2-(fluoromethoxy)-1-phenylvinyl)benzene (12).



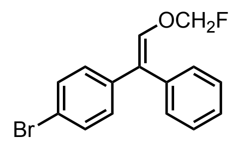
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (26.6 mg, 54% yield, 1.3:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.28 - 7.09 (m, 7H), 6.97 - 6.88 (m, 2H), 6.56 (d, J = 12.4 Hz, 1H), 5.41 (dd, J = 54.4 Hz, 2.4 Hz, 2H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, $CDCl_3$):** δ 163.4 (d, J = 36.2 Hz), 141.3, 139.3, 135.5 (d, J = 3.2 Hz), 131.8 (d, J = 7.9 Hz), 130.0, 128.6, 127.5, 124.2, 115.4 (d, J = 21.5 Hz), 102.6 (d, J = 222.5 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -115.4 (s, 1F), -150.0 (s, 1F) ppm; **Data of the other isomer: ^{13}C NMR (101 MHz, $CDCl_3$):** δ 160.9 (d, J = 36.5 Hz), 141.1, 136.7, 132.8 (d, J = 3.4 Hz), 130.0 (d, J = 8.0 Hz), 128.32, 128.25, 127.5, 124.1, 115.1 (d, J = 21.3 Hz), 102.6 (d, J = 222.5 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -114.7 (s, 1F), -149.9 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{15}H_{12}F_2NaO$ $[M+Na]^+$: 269.0748; found: 269.0749.

1-Chloro-4-(2-(fluoromethoxy)-1-phenylvinyl)benzene (13).



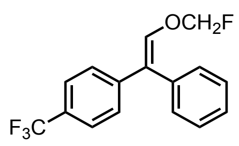
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (27.3 mg, 52% yield, 1.7:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.30 - 7.09 (m, 9H), 6.62 (s, 1H), 5.45 (d, *J* = 54.8 Hz, 2H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.6, 139.0, 136.4, 133.1, 131.5, 130.1, 128.7, 128.4, 127.6, 124.1, 102.6 (d, *J* = 222.8 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -150.0 ppm; **Data of the other isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.4, 138.0, 135.3, 133.1, 129.6, 128.6, 128.4, 128.3, 127.5, 124.0, 102.6 (d, *J* = 222.8 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -149.9 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{15}H_{12}ClFNaO$ [M+Na]$^+$: 285.0453; found: 285.0459.

1-Bromo-4-(2-(fluoromethoxy)-1-phenylvinyl)benzene (14).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (29.4 mg, 48% yield, 1.5:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.40 - 7.33 (m, 2H), 7.28 - 7.00 (m, 7H), 6.60 (s, 1H), 5.42 (d, *J* = 54.4 Hz, 2H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.6, 138.9, 135.8, 131.8, 131.6, 130.1, 128.6, 127.5, 124.0, 121.3, 102.6 (d, *J* =222.9 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -149.9 ppm; **Data of the other isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.4, 138.5, 136.3, 131.3, 129.9, 128.4, 128.3, 127.6, 124.2, 121.3, 102.6 (d, *J* = 222.9 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -150.1 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{15}H_{13}BrFO$ [M+H]$^+$: 307.0128; found: 307.0113.

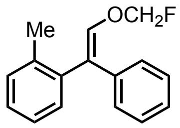
1-(2-(Fluoromethoxy)-1-phenylvinyl)-4-(trifluoromethyl)benzene (15).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (30.8 mg, 52% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.44 (d, *J* = 8.4 Hz, 2H), 7.31 - 7.14 (m, 5H), 6.68 (s, 1H), 5.47 (d, *J* = 54.4 Hz, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 142.3, 140.6, 138.7, 130.4, 129.2 (d, *J* = 32.5 Hz), 128.7, 128.4, 127.7, 125.1 (q, *J* = 3.7 Hz), 124.3 (q, *J* = 273.2 Hz), 123.9, 102.6 (d, *J* = 223.3 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -62.5 (s, 3F), -150.0 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{16}H_{13}F_4O$ [M+H]$^+$:

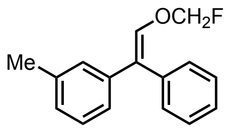
297.0897; found: 297.0910.

1-(2-(Fluoromethoxy)-1-phenylvinyl)-2-methylbenzene (16).



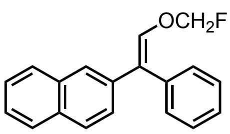
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (16.9 mg, 35% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.35 - 7.33 (m, 2H), 7.26 - 7.12 (m, 7H), 6.39 (s, 1H), 5.48 (d, J = 54.8 Hz, 2H), 2.00 (s, 3H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 142.1, 138.5, 138.2, 136.7, 131.3, 130.4, 129.0, 128.2, 127.9, 127.0, 125.9, 123.5, 102.7 (d, J = 222.3 Hz), 20.3 ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -149.8 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{16}H_{15}FNaO$ $[M+Na]^+$: 265.0999; found: 265.0993.

1-(2-(Fluoromethoxy)-1-phenylvinyl)-3-methylbenzene (17).



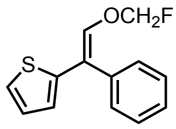
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (20.8 mg, 43% yield, 1.3:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.38 - 7.01 (m, 9H), 6.67 (d, J = 2.4 Hz, 1H), 5.49 (d, J = 54.4 Hz, 2H), 2.32 (d, J = 6.0 Hz, 3H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, $CDCl_3$):** δ 141.2, 139.4, 138.1, 136.9, 130.2, 128.5, 128.25, 128.15, 128.1, 127.3, 125.5, 125.2, 102.6(d, J =223.2 Hz), 21.5 ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -150.0 ppm; **Data of the other isomer: ^{13}C NMR (151 MHz, $CDCl_3$):**δ 141.1, 139.6, 137.8, 136.8, 130.7, 129.0, 128.4, 128.21, 128.15, 127.3, 127.2, 125.2, 102.6 (d, J = 223.2 Hz), 21.6 ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -150.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{16}H_{15}FNaO$ $[M+Na]^+$: 265.0999; found: 265.1001.

2-(2-(Fluoromethoxy)-1-phenylvinyl)naphthalene (18).



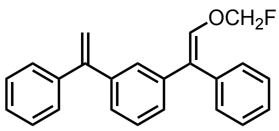
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (26.7 mg, 48% yield, 1:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.79 - 7.64 (m, 4H), 7.47 - 7.20 (m, 8H), 6.77 (s, 0.5H), 6.73 (s, 0.5H), 5.57 – 5.42 (m, 2H) ppm; Data of one isomer:**^{13}C NMR (101 MHz, $CDCl_3$):** δ 141.6, 139.5, 134.4, 133.4, 132.7, 130.3, 129.3, 128.6, 128.3, 128.2, 128.0, 127.5, 127.4, 126.6, 126.1, 126.0, 102.7 (d, J =222.4 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -149.9 ppm; Data of the other isomer:**^{13}C NMR (101 MHz, $CDCl_3$):** δ 141.6, 136.9, 136.8, 133.6, 132.7, 130.3, 129.3, 128.4, 128.0, 127.7, 127.6, 127.4, 126.9, 126.4, 126.1, 125.2, 102.7 (d, J =222.4 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -149.9 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{19}H_{16}FO$ $[M+H]^+$: 279.1180; found: 279.1173.

2-(2-(Fluoromethoxy)-1-phenylvinyl)thiophene (19).



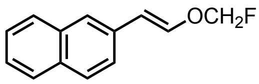
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (20.1 mg, 43% yield, 1.5:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.48 - 7.33 (m, 9H+6H), 7.19 - 7.18 (m, 1H), 7.02 - 6.97 (m, 3H), 6.90 (s, 1H), 6.83 - 6.82 (m, 1H), 6.49 (s, 1.5H), 5.62 (d, J = 54.4 Hz, 3H), 5.49 (d, J = 54.8 Hz, 2H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, $CDCl_3$):** δ 142.3, 140.6, 139.1, 129.9, 128.5, 127.9, 127.4, 126.3, 125.6, 119.7, 102.4 (d, J =223.4 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -150.0 ppm; **Data of the other isomer: ^{13}C NMR (101 MHz, $CDCl_3$):** δ 140.3, 138.2, 136.2, 129.7, 128.2, 127.8, 127.3, 125.9, 123.9, 119.6, 102.5 (d, J = 223.0 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -149.9 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{13}H_{12}FOS$ $[M+H]^+$: 235.0587; found: 235.0580.

1-(2-(Fluoromethoxy)-1-phenylvinyl)-3-(1-phenylvinyl)benzene (20).



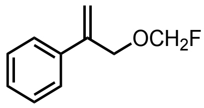
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (23.8 mg, 36% yield, 1:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.41 - 7.24 (m, 14H), 6.69 (d, J = 6.0 Hz, 1H), 5.56 (d, J = 7.6 Hz, 1H), 5.48 - 5.42 (m, 3H) ppm; **Data of one isomer: ^{13}C NMR (151 MHz, $CDCl_3$):** δ 150.0, 141.8, 141.4, 141.3, 139.5, 136.7, 130.1, 129.6, 128.4, 128.3, 128.2, 128.01, 127.96, 127.9, 127.5, 127.4, 125.0, 114.6, 102.6 (d, J = 221.7 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -149.9 ppm; **Data of the other isomer: ^{13}C NMR (151 MHz, $CDCl_3$):** δ 150.0, 141.5, 141.4, 141.3, 139.4, 136.7, 128.5, 128.3, 128.22, 128.18, 128.05, 128.00, 127.9, 127.8, 127.4, 127.3, 125.0, 114.4, 102.6 (d, J =221.7 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -150.1 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{23}H_{20}FO$ $[M+H]^+$: 331.1493; found: 331.1487.

2-(2-(Fluoromethoxy)vinyl)naphthalene (21).



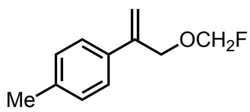
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (6.5 mg, 16% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.12 (d, J = 8.0 Hz, 1H), 7.82 (d, J = 8.4 Hz, 1H), 7.71 - 7.67 (m, 2H), 7.56 - 7.47 (m, 2H), 7.26 - 7.19 (m, 1H), 5.89 (d, J = 18.0 Hz, 1H), 5.74 (d, J = 54.4 Hz, 2H), 5.44 (d, J = 11.2 Hz, 1H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 149.9, 134.5, 131.1, 128.3, 127.9, 126.8, 126.6, 126.4 (d, J = 1.6 Hz), 125.7, 123.2, 122.6, 116.1, 105.1 (d, J =223.6 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -146.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{13}H_{12}FO$ $[M+H]^+$: 203.0867; found: 203.0865.

(3-(Fluoromethoxy)prop-1-en-2-yl)benzene (22).



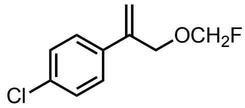
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (20.6 mg, 62% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.49 - 7.46 (m, 2H), 7.39 - 7.30 (m, 3H), 5.61 (s, 1H), 5.41 (s, 1H), 5.35 (d, J = 56.0 Hz, 2H), 4.66 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 142.9, 138.2, 128.6, 128.2, 126.2, 115.8, 102.7 (d, J = 214.7 Hz), 71.6 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{10}H_{12}FO$ $[M+H]^+$: 167.0867; found: 167.0874.

1-(3-(Fluoromethoxy)prop-1-en-2-yl)-4-methylbenzene (23).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (23.4 mg, 65% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.39 - 7.36 (m, 2H), 7.19 - 7.16 (m, 2H), 5.57 (s, 1H), 5.35 (s, 1H), 5.34 (d, J = 56.0 Hz, 2H), 4.64 (s, 2H), 2.36 (s, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 142.7, 138.1, 135.3, 129.3, 126.0, 115.0, 102.6 (d, J = 214.6 Hz), 71.6, 21.3 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{13}FNaO$ $[M+Na]^+$: 203.0843; found: 203.0844.

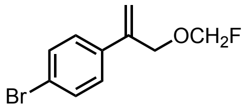
1-Chloro-4-(3-(fluoromethoxy)prop-1-en-2-yl)benzene (24).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (23.2 mg, 58% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.41 (d, J = 8.8 Hz, 2H), 7.33 (d,

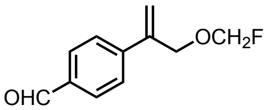
J = 8.4 Hz, 2H), 5.59 (s, 1H), 5.42 (s, 1H), 5.33 (d, J = 56.4 Hz, 2H), 4.61 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.9, 136.6, 134.0, 128.8, 127.5, 116.4, 102.6 (d, J = 215.0 Hz), 71.4 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{10}H_{10}ClFNaO$ $[M+Na]^+$: 223.0296; found: 223.0286.

1-Bromo-4-(3-(fluoromethoxy)prop-1-en-2-yl)benzene (25).



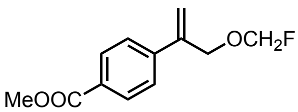
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (27.3 mg, 56% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.48 (d, J = 8.4 Hz, 2H), 7.34 (d, J = 8.8 Hz, 2H), 5.60 (s, 1H), 5.42 (s, 1H), 5.32 (d, J = 56.0 Hz, 2H), 4.61 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.9, 137.0, 131.7, 127.8, 122.2, 116.5, 102.6 (d, J = 215.1 Hz), 71.4 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{10}H_{10}BrFNaO$ $[M+Na]^+$: 266.9791; found: 266.9803.

4-(3-(Fluoromethoxy)prop-1-en-2-yl)benzaldehyde (26)



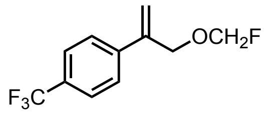
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate= 60: 1). Yellow oil (8.2 mg, 21% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 10.02 (s, 1H), 7.87 (d, J = 8.4 Hz, 2H), 7.63 (d, J = 8.0 Hz, 2H), 5.74 (s, 1H), 5.55 (s, 1H), 5.34 (d, J = 56.0 Hz, 2H), 4.67 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 191.9, 144.2, 142.2, 135.9, 130.1, 126.8, 118.6, 102.7 (d, J =215.3 Hz), 71.3 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.1 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{11}FNaO_2$ $[M+Na]^+$: 217.0635; found: 217.0625.

Methyl 4-(3-(fluoromethoxy)prop-1-en-2-yl)benzoate (27).



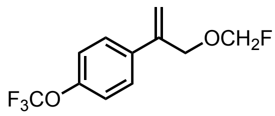
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate= 100: 1). Yellow oil (23.3 mg, 52% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.02 (d, J = 8.4 Hz, 2H), 7.53 (d, J = 8.0 Hz, 2H), 5.70 (s, 1H), 5.50 (s, 1H), 5.33 (d, J = 56.0 Hz, 2H), 4.65 (s, 2H), 3.92 (s, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 166.9, 142.6, 142.2, 129.9, 129.7, 126.2, 117.8, 102.7 (d, J =215.2 Hz), 71.4, 52.3 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.1 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{12}H_{14}FO_3$ $[M+H]^+$: 225.0921; found: 225.0930.

1-(3-(Fluoromethoxy)prop-1-en-2-yl)-4-(trifluoromethyl)benzene (28).



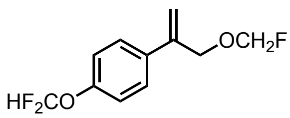
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (21.1 mg, 45% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.63 - 7.60 (m, 2H), 7.58 - 7.56 (m, 2H), 5.67 (s, 1H), 5.51 (s, 1H), 5.33 (d, J = 56.0 Hz, 2H), 4.65 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.9 (d, J = 33.1 Hz), 130.1 (d, J = 32.7 Hz), 126.6, 125.6 (q, J = 3.7 Hz), 121.5 (q, J = 273.0 Hz), 117.9, 115.0, 102.7 (d, J = 215.3 Hz), 71.4 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -62.6 (s, 3F), -153.1 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{10}F_4NaO$ [M+Na]$^+$: 257.0560; found: 257.0566.

1-(3-(Fluoromethoxy)prop-1-en-2-yl)-4-(trifluoromethoxy)benzene (29).



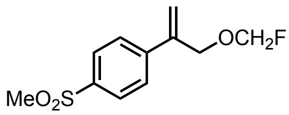
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (28.0 mg, 56% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.50 - 7.47 (m, 2H), 7.21 - 7.19 (m, 2H), 5.59 (s, 1H), 5.43 (s, 1H), 5.33 (d, J = 56.0 Hz, 2H), 4.62 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 149.1, 141.8, 136.9, 127.7, 121.1, 120.6 (q, J = 258.3 Hz), 116.8, 102.6 (d, J = 215.1 Hz), 71.5 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -57.8 (s, 3F), -153.1 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{11}F_4O_2$ [M+H]$^+$: 251.0690; found: 251.0687.

1-(Difluoromethoxy)-4-(3-(fluoromethoxy)prop-1-en-2-yl)benzene (30).



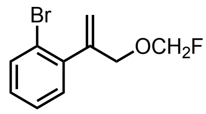
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (28.8 mg, 62% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.49 - 7.45 (m, 2H), 7.11 (d, J = 8.4 Hz, 2H), 6.52 (t, J = 73.6 Hz, 1H), 5.57 (s, 1H), 5.40 (s, 1H), 5.33 (d, J = 56.0 Hz, 2H), 4.62 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 151.1, 141.9, 135.4, 127.7, 119.6, 116.2, 116.0 (t, J = 261.0 Hz), 102.6 (d, J = 214.9 Hz), 71.6 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -80.8 (s, 2F), -153.1 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{12}F_3O_2$ [M+H]$^+$: 233.0784; found: 233.0795.

1-(3-(Fluoromethoxy)prop-1-en-2-yl)-4-(methylsulfonyl)benzene (31).



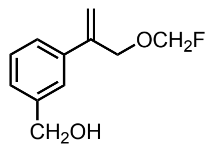
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (27.8 mg, 57% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.94 - 7.91 (m, 2H), 7.67 - 7.64 (m, 2H), 5.72 (s, 1H), 5.57 (s, 1H), 5.33 (d, J = 56.0 Hz, 2H), 4.65 (s, 2H), 3.06 (s, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 143.7, 141.8, 139.9, 127.8, 127.2, 119.2, 102.7 (d, J = 215.7 Hz), 71.3, 44.7 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.1 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{13}FNaO_3S$ $[M+Na]^+$: 267.0462; found: 267.0462.

1-Bromo-2-(3-(fluoromethoxy)prop-1-en-2-yl)benzene (32).



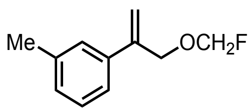
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (15.6 mg, 32% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.57 (d, J = 8.0 Hz, 1H), 7.30 (t, J = 7.6 Hz, 1H), 7.23 - 7.15 (m, 2H), 5.57 - 5.56 (m, 1H), 5.32 (d, J = 56.4 Hz, 2H), 5.23 (s, 1H), 4.53 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 145.0, 140.6, 133.0, 131.0, 129.3, 127.5, 122.3, 118.0, 103.1 (d, J =215.0 Hz), 72.0 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -151.5 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{10}H_{11}BrFO$ $[M+H]^+$: 244.9972; found: 244.9971.

(3-(3-(Fluoromethoxy)prop-1-en-2-yl)phenyl)methanol (33).



Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate= 50: 1). Yellow oil (16.5 mg, 42% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.47 (s, 1H), 7.41 - 7.31 (m, 3H), 5.61 (s, 1H), 5.41 (s, 1H), 5.33 (d, J = 56.4 Hz, 2H), 4.72 (s, 2H), 4.65 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 142.8, 141.2, 138.5, 128.9, 126.8, 125.5, 124.8, 116.1, 102.7 (d, J =214.8 Hz), 71.6, 65.4 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{13}FNaO_2$ $[M+Na]^+$: 219.0792; found: 219.0788.

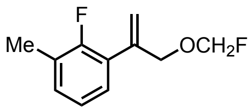
1-(3-(Fluoromethoxy)prop-1-en-2-yl)-3-methylbenzene (34).



Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (22.7 mg, 63% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.31 - 7.28 (m, 3H), 7.18 - 7.15

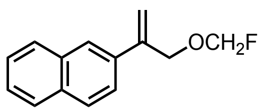
(m, 1H), 5.61 (s, 1H), 5.41 (s, 1H), 5.37 (d, J = 56.4 Hz, 2H), 4.67 (s, 2H), 2.41 (s, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 143.1, 138.2, 129.0, 128.5, 126.9, 123.3, 115.6, 102.7 (d, J = 214.6 Hz), 71.6, 21.6 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -152.9 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{13}FNaO$ [M+Na]$^+$: 203.0843; found: 203.0852.

2-Fluoro-1-(3-(fluoromethoxy)prop-1-en-2-yl)-3-methylbenzene (35).



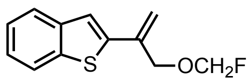
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (9.5 mg, 24% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.16 - 7.12 (m, 2H), 7.03 - 6.99 (m, 1H), 5.53 (s, 1H), 5.44 (s, 1H), 5.31 (d, J = 56.0 Hz, 2H), 4.61 (s, 2H), 2.29 (d, J = 2.4 Hz, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 158.6 (d, J = 247.6 Hz), 140.5, 131.2 (d, J = 5.2 Hz), 127.7 (d, J = 4.2 Hz), 126.5 (d, J = 60.0 Hz), 125.4 (d, J = 18.4 Hz), 123.8 (d, J = 4.1 Hz), 118.4 (d, J = 2.8 Hz), 102.9 (d, J = 214.5 Hz), 72.2 (d, J = 4.8 Hz), 14.8 (d, J = 5.1 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -119.4 (s, 1F), -152.2 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{12}F_2NaO$ [M+Na]$^+$: 221.0748; found: 221.0741.

2-(3-(Fluoromethoxy)prop-1-en-2-yl)naphthalene (36).



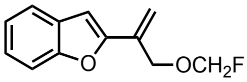
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (22.5 mg, 52% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.91 - 7.82 (m, 4H), 7.65 - 7.63 (m, 1H), 7.52 - 7.46 (m, 2H), 5.77 (s, 1H), 5.51 (s, 1H), 5.39 (d, J = 56.4 Hz, 2H), 4.78 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 142.7, 135.3, 133.4, 133.2, 128.4, 128.2, 127.7, 126.4, 126.3, 125.1, 124.2, 116.3, 102.6 (d, J = 214.7 Hz), 71.6 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{14}H_{14}FO$ [M+H]$^+$: 217.1023; found: 217.1025.

2-(3-(Fluoromethoxy)prop-1-en-2-yl)benzo[*b*]thiophene (37).



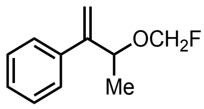
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (12.4 mg, 28% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.78 - 7.76 (m, 1H), 7.73 - 7.71 (m, 1H), 7.34 - 7.31 (m, 3H), 5.73 (s, 1H), 5.45 (s, 1H), 5.39 (d, J = 56.0 Hz, 2H), 4.68 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.8, 140.3, 138.9, 137.2, 125.1, 124.6, 124.0, 122.2, 121.5, 117.0, 102.5 (d, J =215.4 Hz), 71.1 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.4 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{12}H_{12}FOS$ [M+H]$^+$: 223.0587; found: 223.0598.

2-(3-(Fluoromethoxy)prop-1-en-2-yl)benzofuran (38).



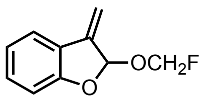
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (12.8 mg, 31% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.55 (d, J = 7.6 Hz, 1H), 7.46 (d, J = 8.4 Hz, 1H), 7.31 - 7.27 (m, 1H), 7.23 - 7.19 (m, 1H), 6.78 (s, 1H), 6.04 (s, 1H), 5.51 (s, 1H), 5.37 (d, J = 56.0 Hz, 2H), 4.62 (s, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 154.8, 153.9, 133.0, 128.8, 125.1, 123.0, 121.4, 116.3, 111.2, 104.0, 102.5 (d, J = 215.2 Hz), 69.9 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.5 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{12}H_{12}FO_2$ [M+H]$^+$: 207.0816; found: 207.0826.

(3-(Fluoromethoxy)but-1-en-2-yl)benzene (39).



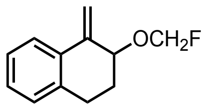
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (12.2 mg, 34% yield, dr = 4.5:1). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.41 - 7.29 (m, 5H+1.1H), 5.46 - 5.30 (m, 4H+0.7H), 4.86 - 4.76 (m, 1H+0.2H), 1.38 - 1.33 (m, 3H+0.7H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 149.0, 139.3, 128.5, 127.9, 127.1, 114.9, 101.7 (d, J =213.2 Hz), 69.7, 21.2 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -151.3 ppm; **Data of the other isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 153.2, 140.0, 128.5, 127.8, 127.0, 111.7, 101.7 (d, J =213.2 Hz), 69.7, 22.7 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.2 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{13}FNaO$ [M+Na]$^+$: 203.0843; found: 203.0843.

2-(Fluoromethoxy)-3-methylene-2,3-dihydrobenzofuran (40).



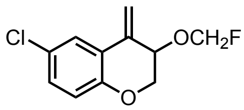
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (25.9 mg, 72% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.35 (d, J = 7.2 Hz, 1H), 7.17 (t, J = 7.2 Hz, 1H), 6.89 (t, J = 7.6 Hz, 1H), 6.82 (d, J = 8.0 Hz, 1H), 6.16 (s, 1H), 5.67 (d, J = 2.0 Hz, 1H), 5.58 (dd, J = 58.0 Hz, 3.2 Hz, 1H), 5.35 (d, J = 1.6 Hz, 1H), 5.34 (dd, J = 51.6 Hz, 2.8 Hz, 1H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 160.7, 142.8, 131.0, 123.9, 121.9, 121.4, 110.8, 108.4, 103.6, 100.4 (d, J = 218.4 Hz) ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.9 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{10}H_{10}FO_2$ [M+H]$^+$: 181.0659; found: 181.0661.

2-(Fluoromethoxy)-1-methylene-1,2,3,4-tetrahydronaphthalene (41).



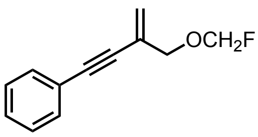
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (17.7 mg, 46% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.63 - 7.61 (m, 1H), 7.24 - 7.12 (m, 3H), 5.71 (s, 1H), 5.43 (dd, *J* = 22.4 Hz, 2.8 Hz, 1H), 5.29 (dd, *J* = 16.0 Hz, 2.8 Hz, 1H), 5.26 (s, 1H), 4.62 - 4.60 (m, 1H), 3.19 - 3.10 (m, 1H), 2.86 - 2.79 (m, 1H), 2.28 - 2.21 (m, 1H), 2.13 - 2.05 (m, 1H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 141.3, 136.3, 132.4, 129.1, 128.3, 126.3, 125.1, 112.5, 101.1 (d, *J* = 212.9 Hz), 77.4, 29.1, 25.4 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -151.4 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{12}H_{13}FNaO$ $[M+Na]^+$: 215.0843; found: 215.0851.

6-Chloro-3-(fluoromethoxy)-4-methylenechromane (42).



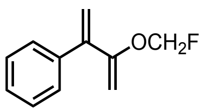
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (25.1 mg, 55% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.49 (d, *J* = 2.4 Hz, 1H), 7.15 (dd, *J* = 8.8 Hz, 2.4 Hz, 1H), 6.83 (d, *J* = 8.8 Hz, 1H), 5.75 (s, 1H), 5.42 - 5.40 (m, 1H), 5.29 - 5.25 (m, 2H), 4.54 - 4.52 (m, 1H), 4.47 (dd, *J* = 12.0 Hz, 3.6 Hz, 1H), 4.22 (dd, *J* = 11.6 Hz, 1.6 Hz, 1H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 152.1, 134.0, 130.1, 126.4, 124.8, 120.6, 118.8, 113.2, 100.5 (d, *J* =215.4 Hz), 72.8, 69.1 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.6 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{10}ClFNaO_2$ $[M+Na]^+$: 251.0246; found: 251.0257.

(3-((Fluoromethoxy)methyl)but-3-en-1-yn-1-yl)benzene (43).



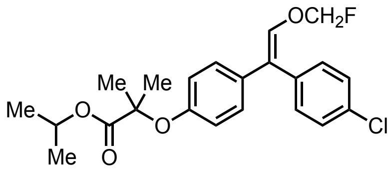
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (16.0 mg, 42% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.47 - 7.45 (m, 2H), 7.33 - 7.32 (m, 3H), 5.66 (q, *J* = 1.2 Hz, 1H), 5.63 (q, *J* = 1.6 Hz, 1H), 5.36 (d, *J* = 56.4 Hz, 2H), 4.35 (q, *J* = 1.6 Hz, 2H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 131.8, 128.7, 128.5, 127.2, 123.1, 122.8, 102.9 (d, *J* = 215.6 Hz), 90.7, 87.0, 71.8 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -152.2 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{12}H_{12}FO$ $[M+H]^+$: 191.0867; found: 191.0858.

(3-(Fluoromethoxy)buta-1,3-dien-2-yl)benzene (44).



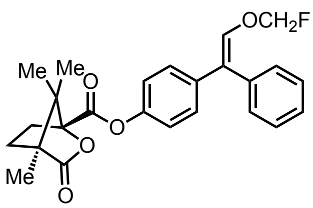
Prepared according to the general procedure **D** and purified by column chromatography (hexane). Yellow oil (9.3 mg, 26% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.36 - 7.32 (m, 5H), 5.72 (s, 2H), 5.58 (s, 1H), 5.28 (s, 1H), 4.79 (s, 1H), 4.46 (d, J = 2.8 Hz, 1H) ppm; **^{13}C NMR (101 MHz, $CDCl_3$):** δ 158.8 (d, J = 3.0 Hz), 144.5 (d, J = 1.6 Hz), 139.7, 128.8, 128.2, 127.9, 116.2, 99.9 (d, J = 218.7 Hz), 93.9 (d, J = 1.5 Hz) ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -150.1 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{11}H_{12}FO$ $[M+H]^+$: 179.0867; found: 179.0863.

Isopropyl-2-(4-(1-(4-chlorophenyl)-2-(fluoromethoxy)vinyl)phenoxy)-2-methylpropanoate (45).



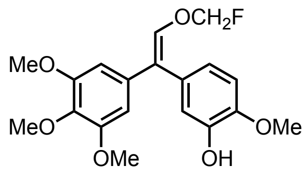
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate= 80: 1). Yellow oil (45.5 mg, 56% yield, 1.1:1 mixture of *E* and *Z* isomers). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.24 - 7.18 (m, 3H), 7.12 - 7.09 (m, 1H), 7.04 - 7.00 (m, 1H), 6.78 - 6.73 (m, 2H), 6.56 (d, J = 12.8 Hz, 1H), 5.43 (dd, J = 54.8 Hz, 5.2 Hz, 2H), 5.08 - 5.02 (m, 1H), 1.57 (s, 3H), 1.56 (s, 3H), 1.19 (d, J = 2.0 Hz, 3H), 1.18 (d, J = 1.6 Hz, 3H) ppm; **Data of one isomer: ^{13}C NMR (151 MHz, $CDCl_3$):** δ 173.8, 154.9, 140.9, 138.3, 133.1, 132.5, 130.8, 129.8, 128.6, 123.6, 118.4, 102.6 (d, J = 221.8 Hz), 79.3, 69.1, 25.6, 21.7 ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -150.0 ppm; **Data of the other isomer: ^{13}C NMR (151 MHz, $CDCl_3$):** δ 173.8, 155.2, 140.9, 135.5, 133.0, 132.5, 131.5, 129.0, 128.4, 123.5, 118.9, 102.6 (d, J = 221.8 Hz), 79.2, 69.1, 25.5, 21.7 ppm; **^{19}F NMR (376 MHz, $CDCl_3$):** δ -149.9 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{22}H_{24}ClFNaO_4$ $[M+Na]^+$: 429.1239; found: 429.1238.

4-(2-(Fluoromethoxy)-1-phenylvinyl)phenyl (4*R*)-4,7,7-trimethyl-3-oxo-2-oxabicyclo[2.2.1]heptane-1-carboxylate (46).



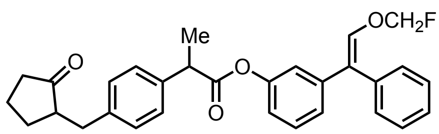
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (15.3 mg, 18% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.43 - 7.41 (m, 2H), 7.34 - 7.28 (m, 3H), 7.24 - 7.22 (m, 2H), 7.13 - 7.11 (m, 2H), 6.68 (s, 1H), 5.51 (d, J = 54.8 Hz, 2H), 2.61 - 2.54 (m, 1H), 2.24 - 2.17 (m, 1H), 2.05 - 1.96 (m, 1H), 1.81 - 1.74 (m, 1H), 1.17 (s, 3H), 1.16 (s, 3H), 1.11 (s, 3H) ppm; **^{13}C NMR (151 MHz, $CDCl_3$):** δ 178.1, 166.2, 149.0, 141.6, 139.1, 135.2, 131.4, 128.6, 128.4, 127.5, 124.1, 121.0, 102.6 (d, J =222.0 Hz), 91.0, 55.1, 54.8, 30.9, 29.1, 17.0, 9.9 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -150.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{25}H_{25}FNaO_5$ $[M+Na]^+$: 447.1578; found: 447.1566.

5-(2-(Fluoromethoxy)-1-(3,4,5-trimethoxyphenyl)vinyl)-2-methoxyphenol (47).



Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate= 20: 1).Yellow oil (15.3 mg, 21% yield, 1.2:1 mixture of *E* and *Z* isomers). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 6.90 - 6.71 (m, 3H), 6.61 - 6.59 (m, 2H), 6.44 (s, 1H), 5.59 (s, 1H), 5.51 (dd, J = 54.4 Hz, 5.2 Hz, 2H), 3.90 (d, J = 4.0 Hz, 3H), 3.87 (d, J = 7.6 Hz, 3H), 3.80 (d, J = 2.4 Hz, 6H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 153.2, 145.9, 145.1, 140.6, 137.6, 135.4, 132.7, 124.7, 122.1, 116.4, 110.3, 106.0, 102.6 (d, J = 221.5 Hz), 61.1, 56.3, 56.0 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -150.0 ppm; **Data of the other isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 152.9, 146.2, 145.5, 140.4, 137.3, 135.4, 132.4, 125.0, 120.0, 114.4, 110.6, 107.5, 102.7 (d, J = 221.4 Hz), 61.0, 56.2, 56.1 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -149.9 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{19}H_{21}FNaO_6$ $[M+Na]^+$: 387.1214; found: 387.1221.

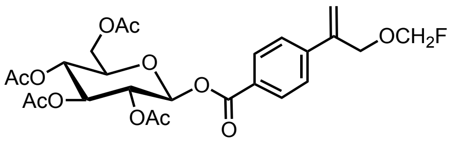
4-(2-(Fluoromethoxy)-1-phenylvinyl)phenyl 2-(4-((2-oxocyclopentyl)methyl)phenyl)propanoate (48).



Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate = 60: 1). Yellow oil (43.4 mg, 46% yield, 1.1:1 mixture of E and Z isomers). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.28 - 7.18 (m, 6H), 7.14 - 7.04 (m, 5H), 6.92 - 6.85 (m, 2H), 6.58 - 6.57 (m, 1H), 5.42 (dd, J = 54.8 Hz, 3.2 Hz, 2H), 3.89 - 3.85 (m, 1H), 3.10 - 3.05 (m, 1H), 2.49 - 2.43 (m, 1H), 2.31 - 2.24 (m, 2H), 2.09 - 2.06 (m, 2H), 1.93 - 1.85 (m, 1H), 1.70 - 1.62 (m, 1H), 1.54 - 1.52 (m, 3H), 1.49 - 1.45 (m, 1H) ppm; **Data of one isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 220.4, 173.2, 150.1, 141.4, 138.0, 137.1, 134.4, 131.1, 129.5, 129.43, 129.42, 129.2, 127.7, 127.5, 124.2, 121.4, 102.6 (d, J = 222.6 Hz), 51.1, 45.4, 38.3, 35.3, 29.3, 20.7, 18.6 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -150.0 ppm; **Data of the other isomer: ^{13}C NMR (101 MHz, CDCl$_3$):** δ 220.3, 173.2, 149.9, 141.3, 137.9, 136.6, 131.7, 130.1, 128.5, 128.45, 128.36, 128.2, 127.7, 127.4, 124.2, 121.0, 102.6 (d, J = 222.6 Hz), 51.1, 45.4, 38.3, 35.3, 29.3, 20.7, 18.6 ppm;

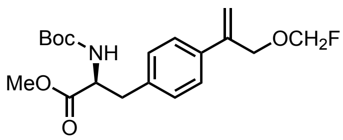
^{19}F NMR (376 MHz, CDCl$_3$): δ -150.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{30}H_{29}FNaO_4$ [M+Na]$^+$: 495.1942; found: 495.1933.

(2*R*,3*R*,4*S*,5*R*,6*R*)-2-(Acetoxymethyl)-6-((4-(3-(fluoromethoxy)prop-1-en-2-yl)benzoyl)oxy)tetrahydro-2*H*-pyran-3,4,5-triyl triacetate (49).



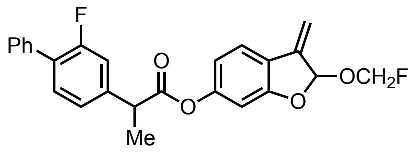
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate = 10: 1). Yellow oil (48.6 mg, 45% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.4 Hz, 2H), 5.92 - 5.90 (m, 1H), 5.69 (s, 1H), 5.51 (s, 1H), 5.38 (s, 1H), 5.35 - 5.32 (m, 2H), 5.24 (s, 1H), 5.21 - 5.16 (m, 1H), 4.63 (s, 2H), 4.34 - 4.30 (m, 1H), 4.14 - 4.11 (m, 1H), 3.96 - 3.91 (m, 1H), 2.06 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 1.98 (s, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 170.7, 170.2, 169.6, 169.5, 164.3, 143.7, 142.1, 130.5, 127.9, 126.4, 118.3, 102.6 (d, *J* = 215.3 Hz), 92.4, 72.9, 72.7, 71.3, 70.2, 68.0, 61.6, 20.8, 20.70, 20.68, 20.66 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{25}H_{29}FNaO_{12}$ [M+Na]$^+$: 563.1535; found: 563.1533.

Methyl 2-((*tert*-butoxycarbonyl)amino)-3-(4-(3-(fluoromethoxy)prop-1-en-2-yl)phenyl)propanoate (50).



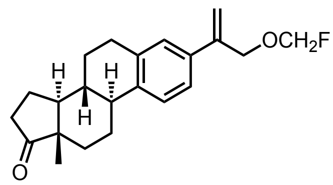
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate = 30: 1). Yellow oil (23.5 mg, 32% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.40 - 7.38 (m, 2H), 7.12 - 7.10 (m, 2H), 5.58 (s, 1H), 5.37 (s, 1H), 5.33 (d, *J* = 56.0 Hz, 2H), 4.99 - 4.97 (m, 1H), 4.62 (s, 2H), 3.72 (s, 3H), 3.15 - 3.01 (m, 2H), 1.42 (s, 9H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 172.4, 155.2, 142.4, 136.9, 136.1, 129.6, 126.3, 115.7, 102.6 (d, *J* = 214.7 Hz), 80.1, 71.5, 54.4, 52.4, 38.1, 28.4 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{19}H_{26}FNNaO_5$ [M+Na]$^+$: 390.1687; found: 390.1679.

2-(Fluoromethoxy)-3-methylene-2,3-dihydrobenzofuran-5-yl 2-(2-fluoro-[1,1'-biphenyl]-4-yl)propanoate (51).



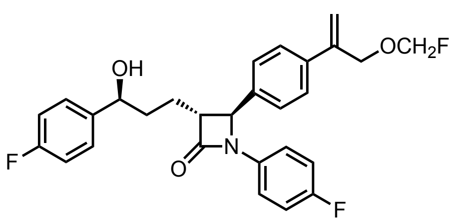
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate= 30: 1). Yellow oil (43.9 mg, 52% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.49 - 7.47 (m, 2H), 7.39 - 7.34 (m, 3H), 7.31 - 7.28 (m, 2H), 7.17 - 7.11 (m, 2H), 6.58 - 6.53 (m, 2H), 6.16 (s, 1H), 5.63 (s, 1H), 5.54 (dd, *J* = 58.8 Hz, 2.4 Hz, 1H), 5.33 (s, 1H), 5.32 (dd, *J* = 51.6 Hz, 2.0 Hz, 1H), 3.90 (q, *J* = 7.2 Hz, 1H), 1.56 (d, *J* = 7.2 Hz, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 172.3, 161.3, 159.9 (d, *J* = 249.9 Hz), 152.9, 141.8, 141.2 (d, *J* = 7.7 Hz), 135.5, 131.2 (d, *J* = 4.0 Hz), 129.1 (d, *J* = 2.8 Hz), 128.6, 128.3 (d, *J* =13.8 Hz), 127.9, 123.7 (d, *J* = 3.5 Hz), 121.9, 121.6, 115.4 (d, *J* = 23.8 Hz), 115.1, 108.4, 104.9, 104.4, 100.3 (d, *J* = 219.9 Hz), 45.3, 18.5 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -117.165 - -117.169 (m, 1F), -154.19 - -154.23 (m, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{25}H_{20}F_2NaO_4$ $[M+Na]^+$: 445.1222; found: 445.1199.

(8*R*,9*S*,13*S*,14*S*)-3-(3-(Fluoromethoxy)prop-1-en-2-yl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17*H*-cyclopenta[*a*]phenanthren-17-one (52).



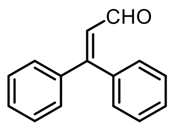
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate = 50: 1). Yellow oil (28.7 mg, 42% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.36 - 7.30 (m, 3H), 5.62 (s, 1H), 5.41 (s, 1H), 5.39 (d, *J* = 56.0 Hz, 2H), 4.69 (s, 2H), 3.01 - 2.98 (m, 2H), 2.61 - 2.54 (m, 1H), 2.52 - 2.47 (m, 1H), 2.40 - 2.34 (m, 1H), 2.23 - 2.02 (m, 4H), 1.73 - 1.52 (m, 6H), 0.97 (s, 3H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 220.9, 142.7, 139.9, 136.7, 135.7, 126.7, 125.7, 123.6, 115.2, 102.6 (d, *J* = 214.6 Hz), 71.5, 50.6, 48.1, 44.5, 38.2, 36.0, 31.7, 29.6, 26.6, 25.8, 21.7, 14.0 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -153.0 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{22}H_{28}FO_2$ $[M+H]^+$: 343.2068; found: 343.2082.

(3*R*,4*S*)-4-(4-(3-(fluoromethoxy)prop-1-en-2-yl)phenyl)-1-(4-fluorophenyl)-3-((*S*)-3-(4-fluorophenyl)-3-hydroxypropyl)azetidin-2-one (53).



Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate = 20: 1). Yellow oil (36.6 mg, 38% yield). **^{1}H NMR (400 MHz, CDCl$_3$):** δ 7.48 (d, *J* = 8.4 Hz, 2H), 7.31 - 7.28 (m, 4H), 7.24 - 7.21 (m, 2H), 7.00 (t, *J* = 8.8 Hz, 2H), 6.92 (t, *J* = 8.8 Hz, 2H), 5.61 (s, 1H), 5.42 (s, 1H), 5.32 (d, *J* = 56.0 Hz, 2H), 4.70 (t, *J* = 5.2 Hz, 1H), 4.63 (s, 1H), 4.62 (s, 2H), 3.08 (t, *J* = 6.0 Hz, 1H), 2.63 (s, 1H), 2.03 - 1.86 (m,4H) ppm; **^{13}C NMR (101 MHz, CDCl$_3$):** δ 167.6, 162.3 (d, *J* =246.3 Hz), 159.1 (d, *J* =244.4 Hz), 142.1, 140.2 (d, *J* =3.1 Hz), 138.5, 137.4, 133.9 (d, *J* =2.7 Hz), 127.5 (d, *J* =8.1 Hz), 127.0, 126.1, 118.5 (d, *J* =7.8 Hz), 116.6, 116.0 (d, *J* =22.8 Hz), 115.4 (d, *J* =21.4 Hz), 102.6 (d, *J* =215.1 Hz), 73.1, 71.5, 61.2, 60.4, 36.7, 25.1 ppm; **^{19}F NMR (376 MHz, CDCl$_3$):** δ -114.8 (s, 1F), -117.9 (s, 1F), -153.0 (s, 1F) ppm; **HRMS** (m/z) (ESI): calcd. for $C_{28}H_{26}F_3NNaO_3$ $[M+Na]^+$: 504.1757; found: 504.1755.

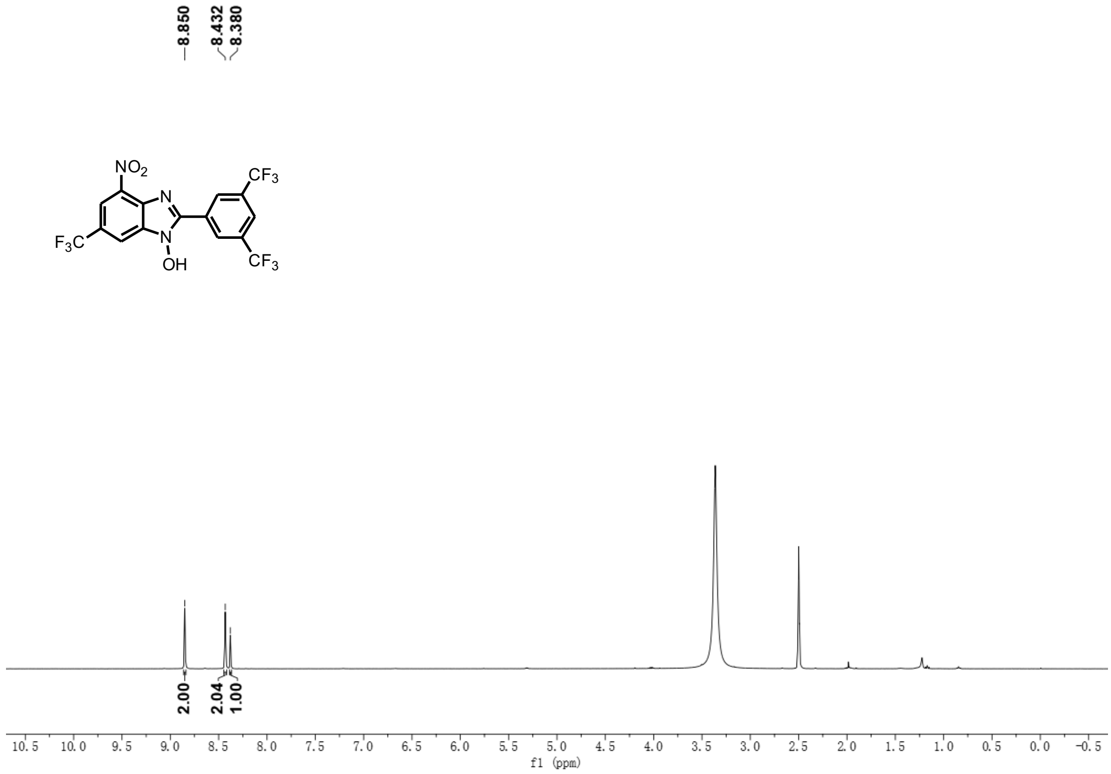
3,3-diphenylacrylaldehyde (3').



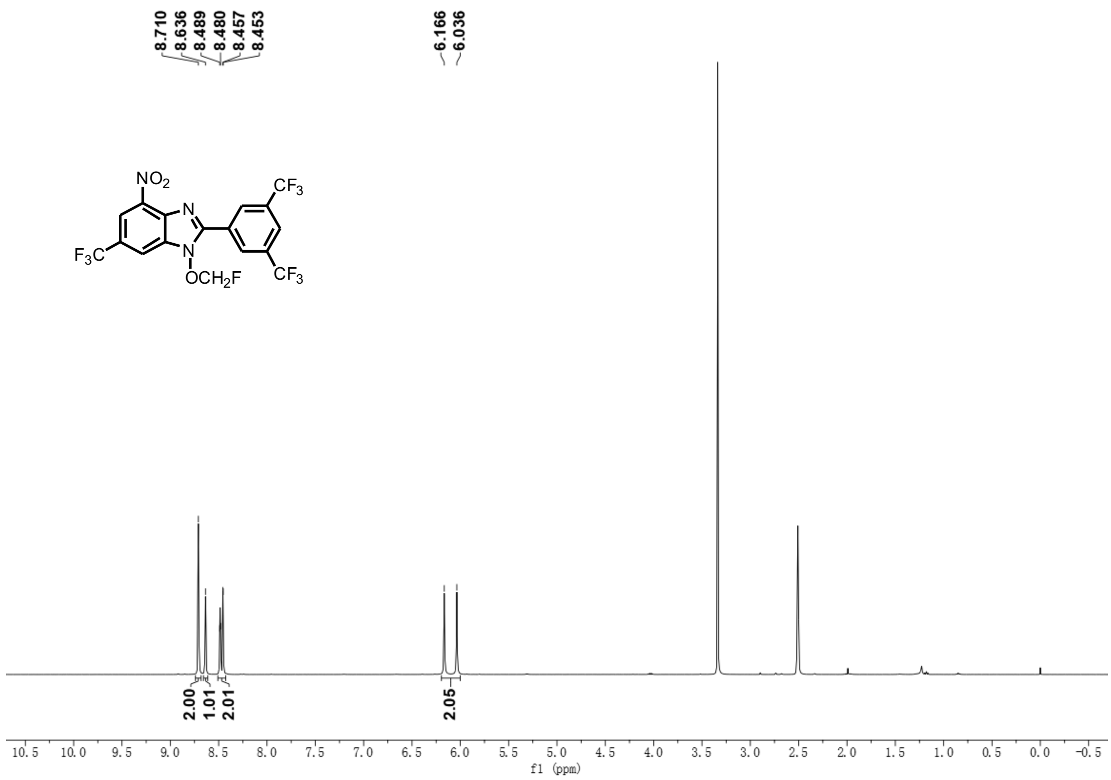
Prepared according to the general procedure **D** and purified by column chromatography (hexane: ethyl acetate = 100: 1). Yellow oil (3.3 mg, 8% yield). **^{1}H NMR (600 MHz, CDCl$_3$):** δ 9.53 (d, *J* = 7.8 Hz, 1H), 7.50 - 7.42 (m, 4H), 7.40 - 7.35 (m, 4H), 7.32 - 7.31 (m, 2H), 6.60 (d, *J* = 7.8 Hz, 1H) ppm; **^{13}C NMR (151 MHz, CDCl$_3$):** δ 193.7, 162.4, 139.9, 136.8, 130.9, 130.6, 129.6, 128.83, 128.78, 128.5, 127.4 ppm; **HRMS** (m/z) (ESI): calcd. for $C_{15}H_{12}NaO$ $[M+Na]^+$: 231.0780; found: 231.0781.

13. Spectra

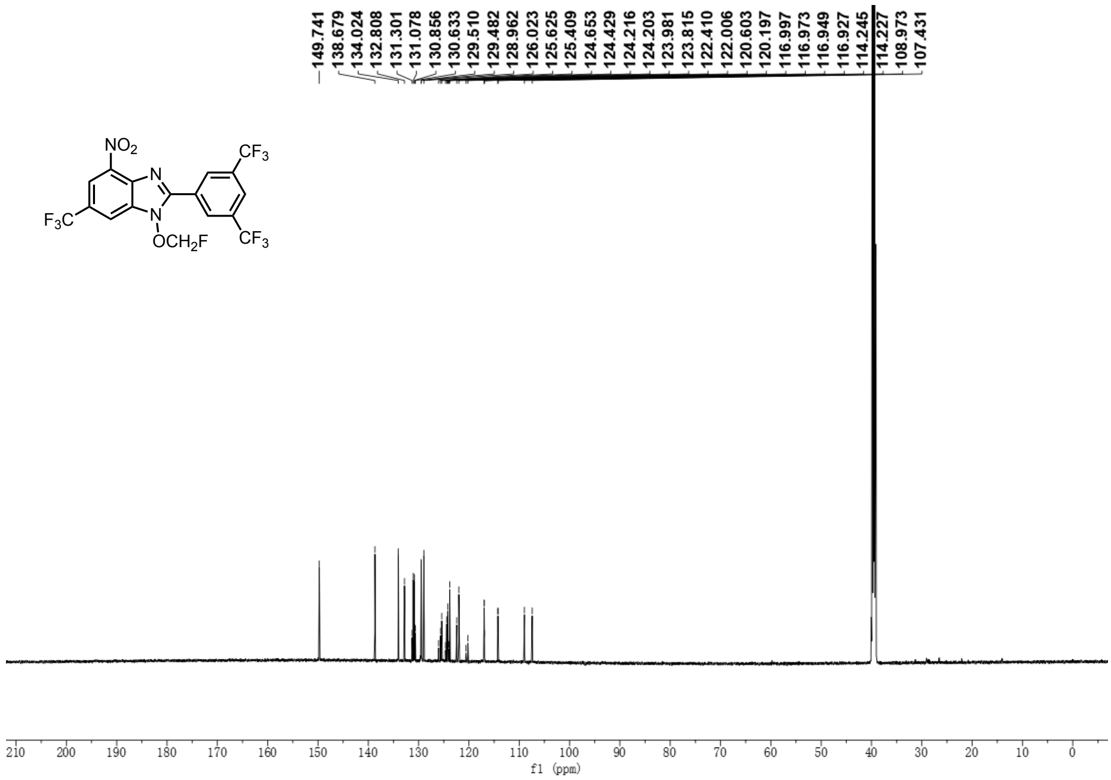
^{1}H NMR Spectrum of Compound **S1** (400 MHz, DMSO-d_6)



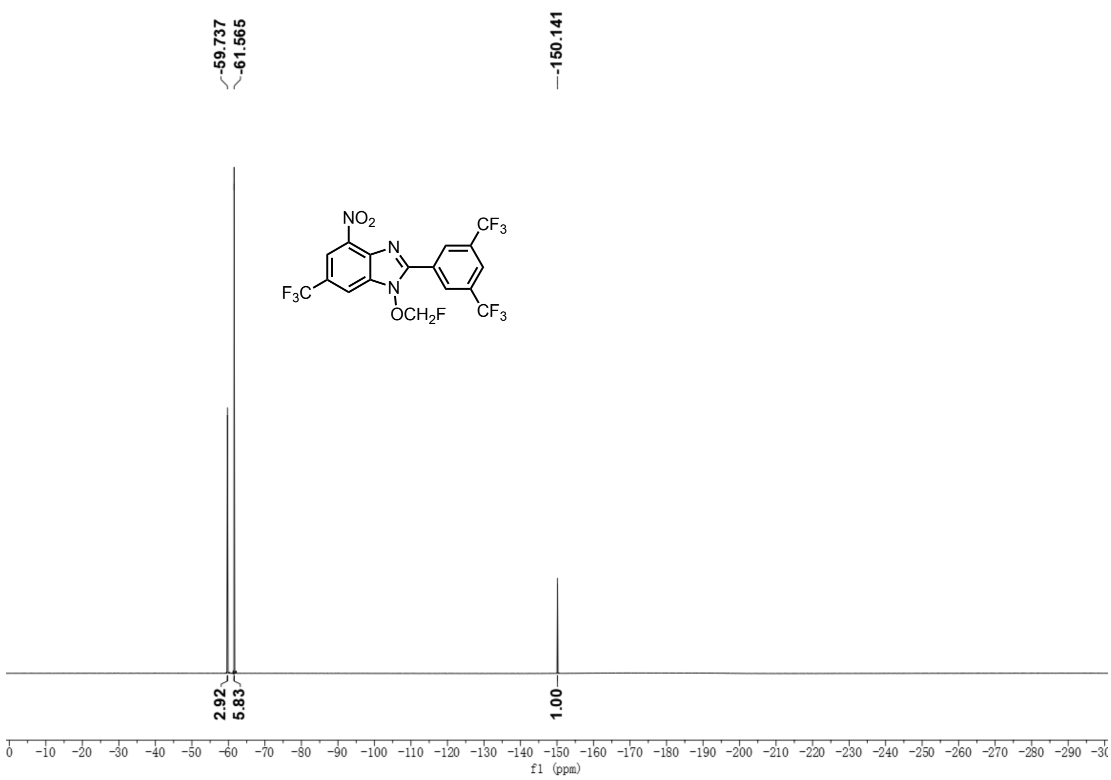
^{1}H NMR Spectrum of Compound **1** (400 MHz, DMSO-d_6)



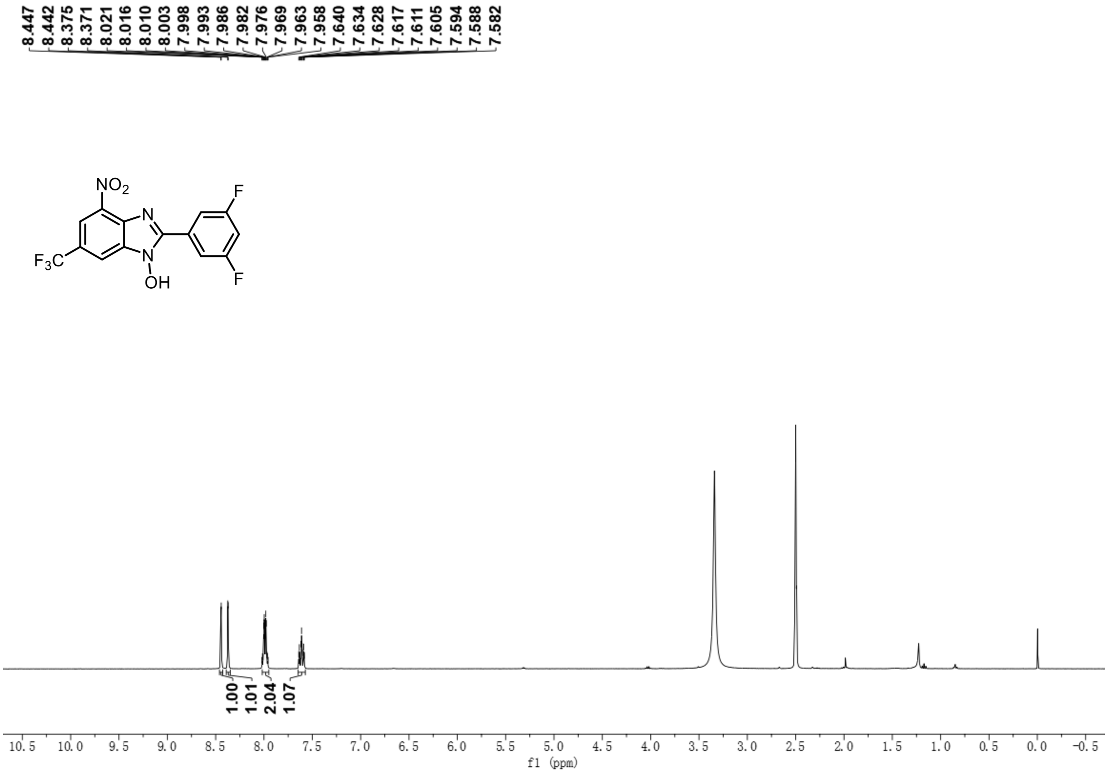
^{13}C NMR Spectrum of Compound **1** (151 MHz, DMSO-d_6)



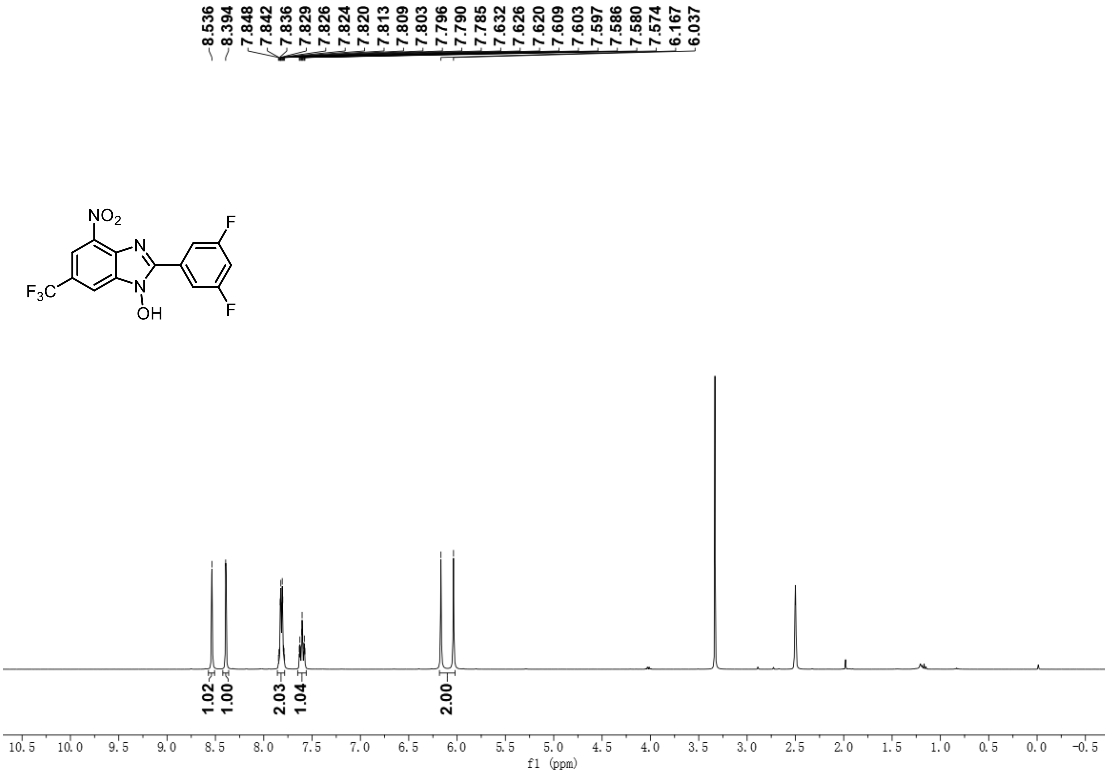
^{19}F NMR Spectrum of Compound **1** (376 MHz, DMSO-d_6)



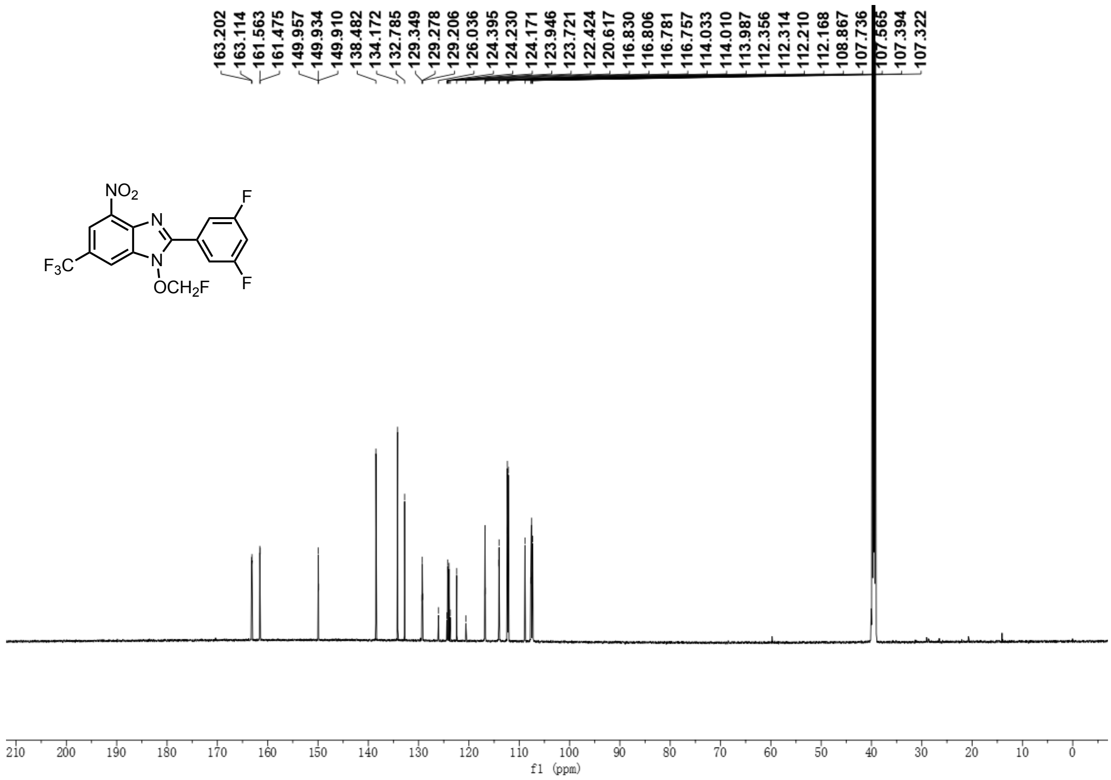
^{1}H NMR Spectrum of Compound **S1a** (400 MHz, DMSO-d_6)



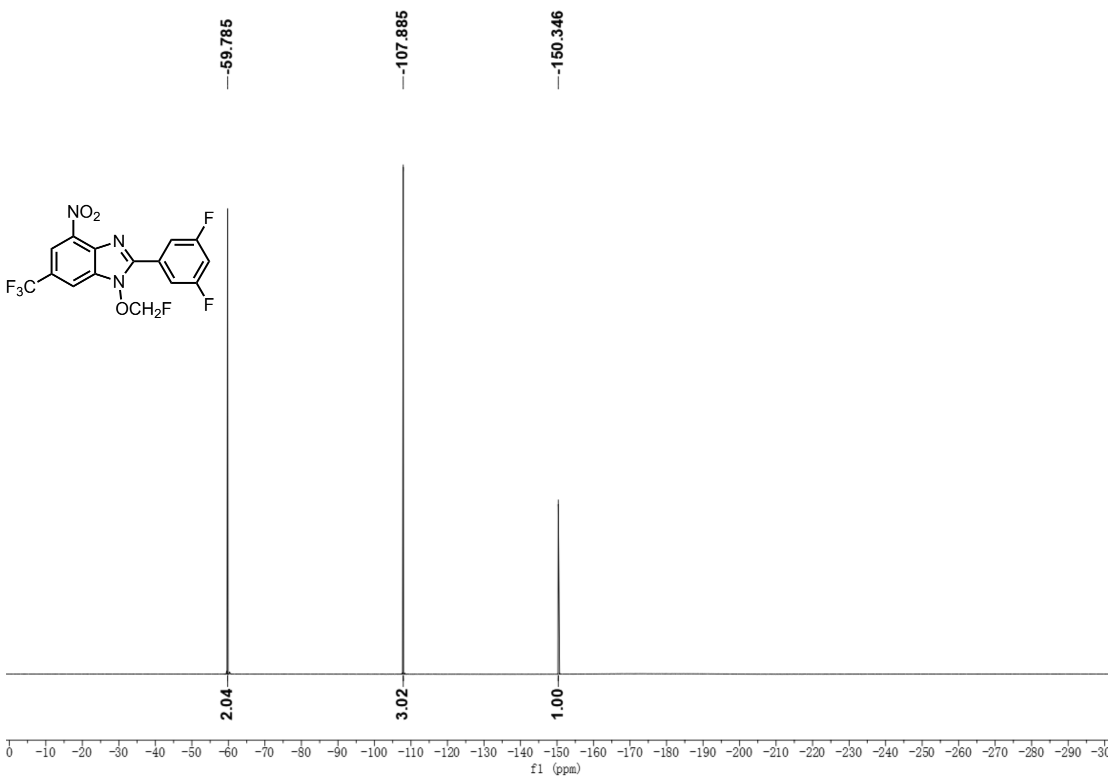
^{1}H NMR Spectrum of Compound **1a** (400 MHz, DMSO-d_6)



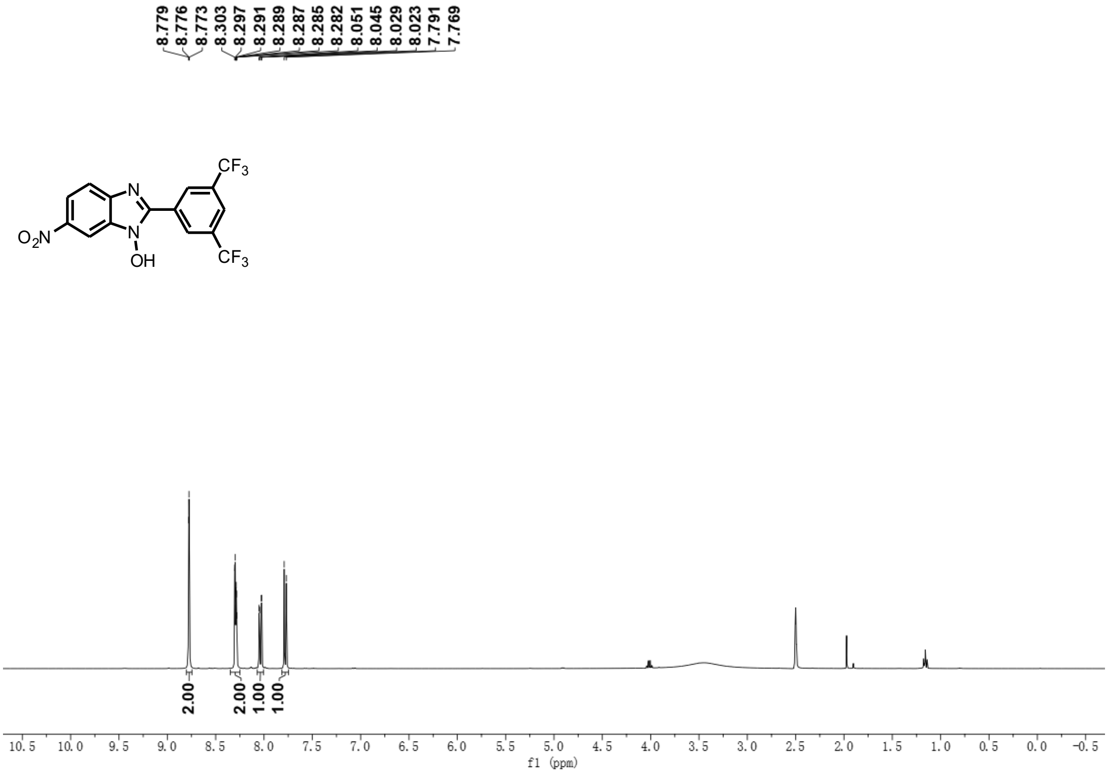
^{13}C NMR Spectrum of Compound **1a** (151 MHz, DMSO-d_6)



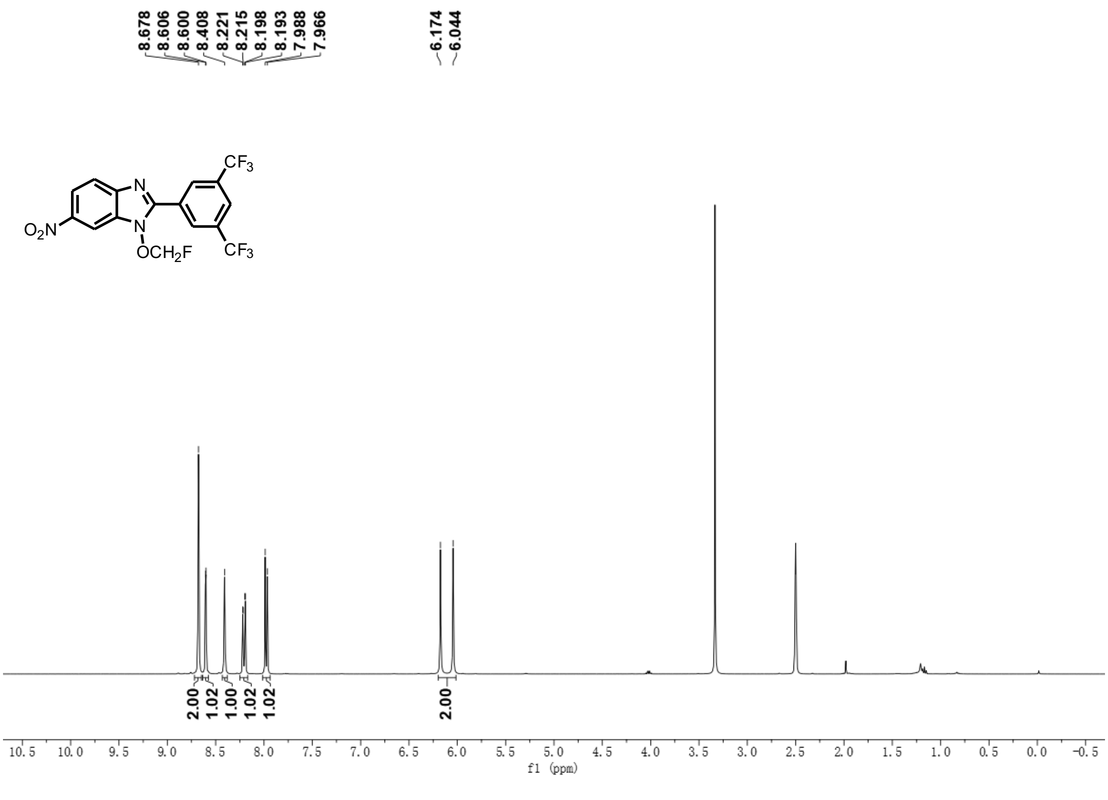
^{19}F NMR Spectrum of Compound **1a** (376 MHz, DMSO-d_6)



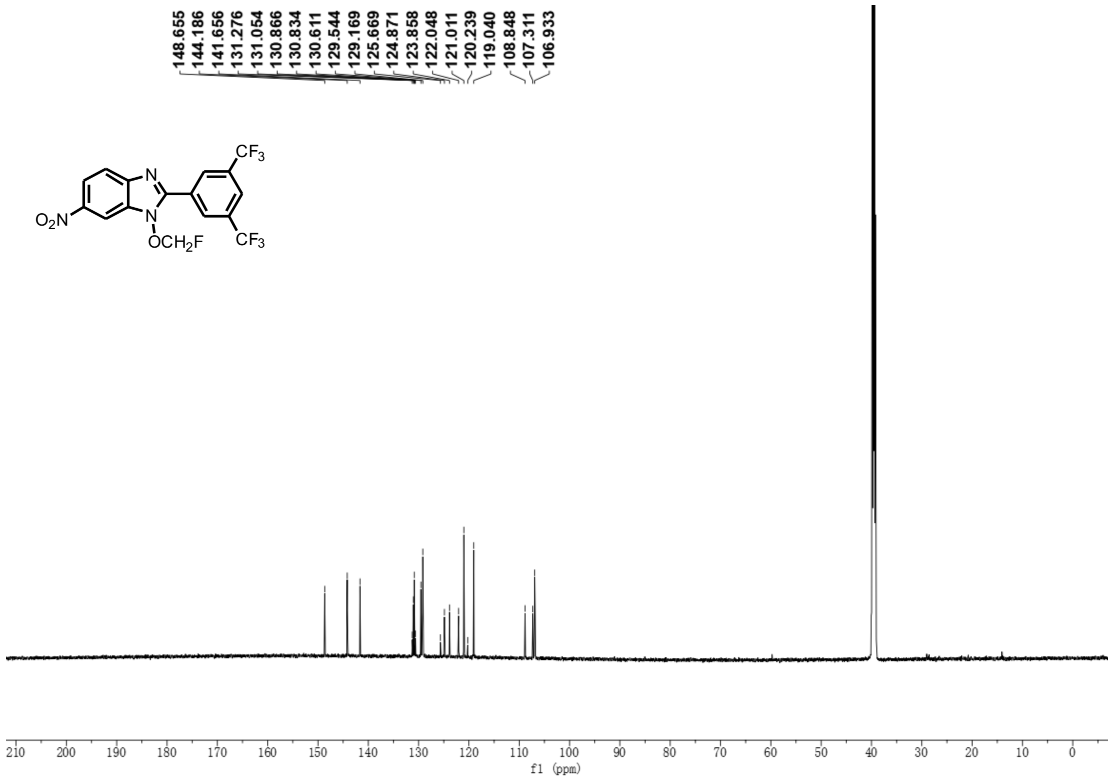
^{1}H NMR Spectrum of Compound **S1b** (400 MHz, DMSO-d_6)



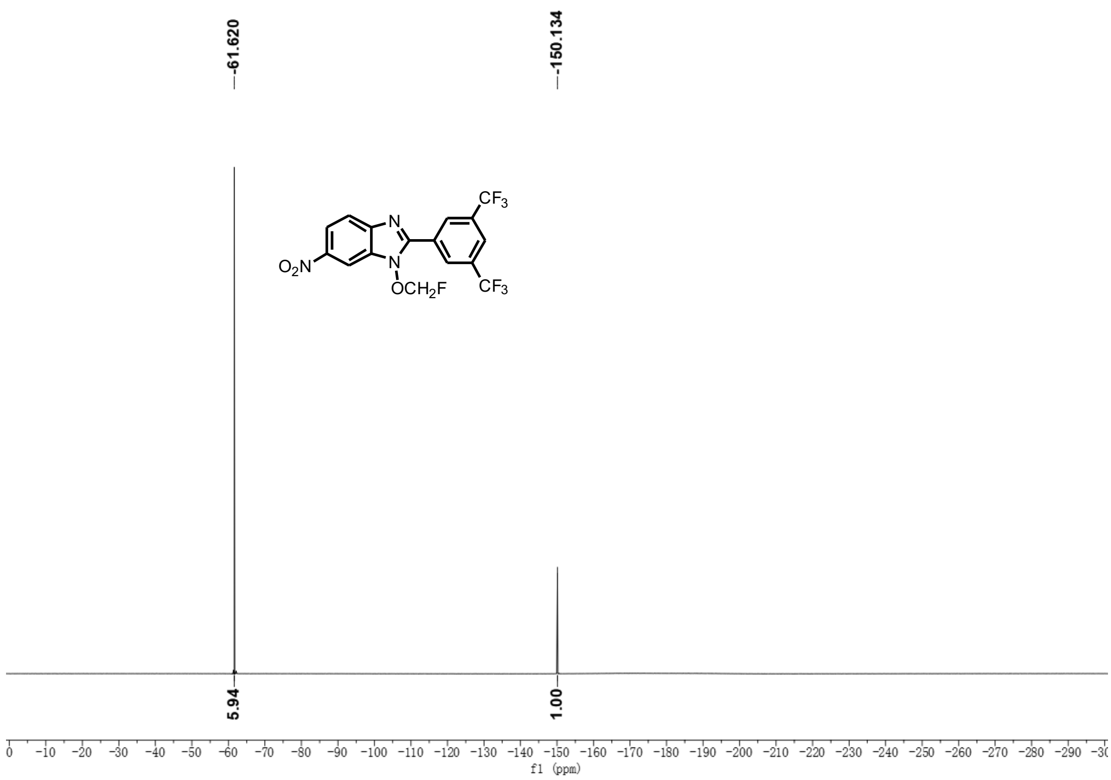
^{1}H NMR Spectrum of Compound **1b** (400 MHz, DMSO-d_6)



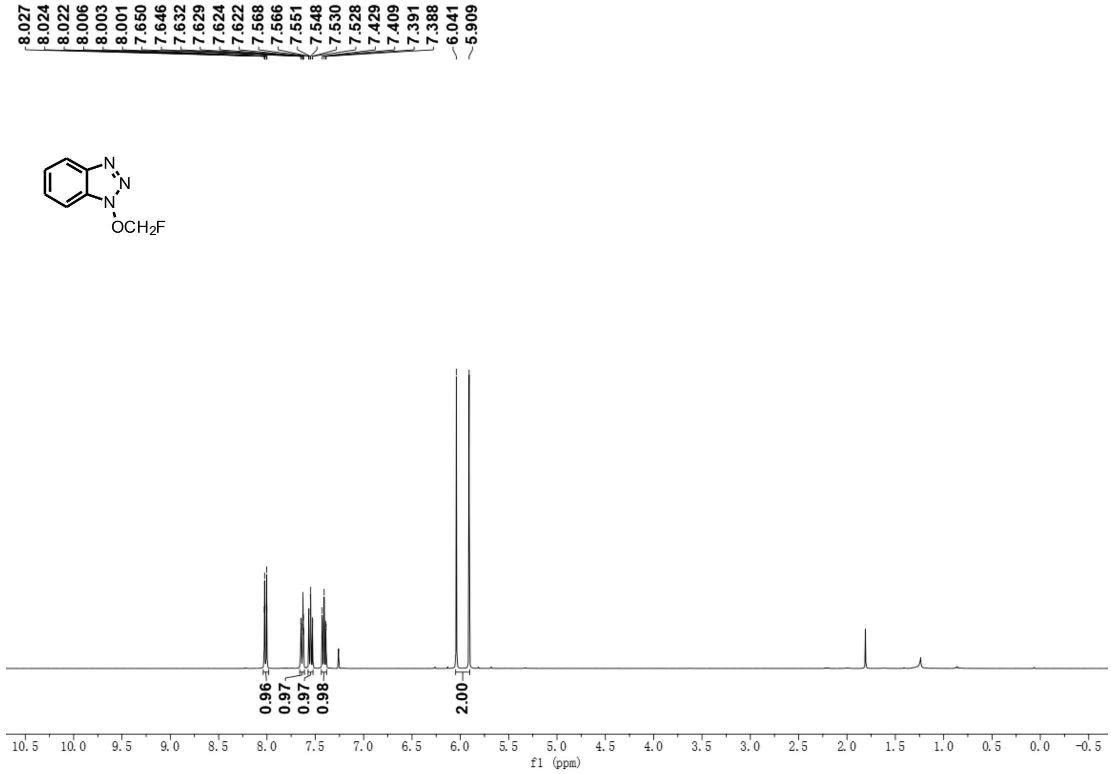
^{13}C NMR Spectrum of Compound **1b** (151 MHz, DMSO-d_6)



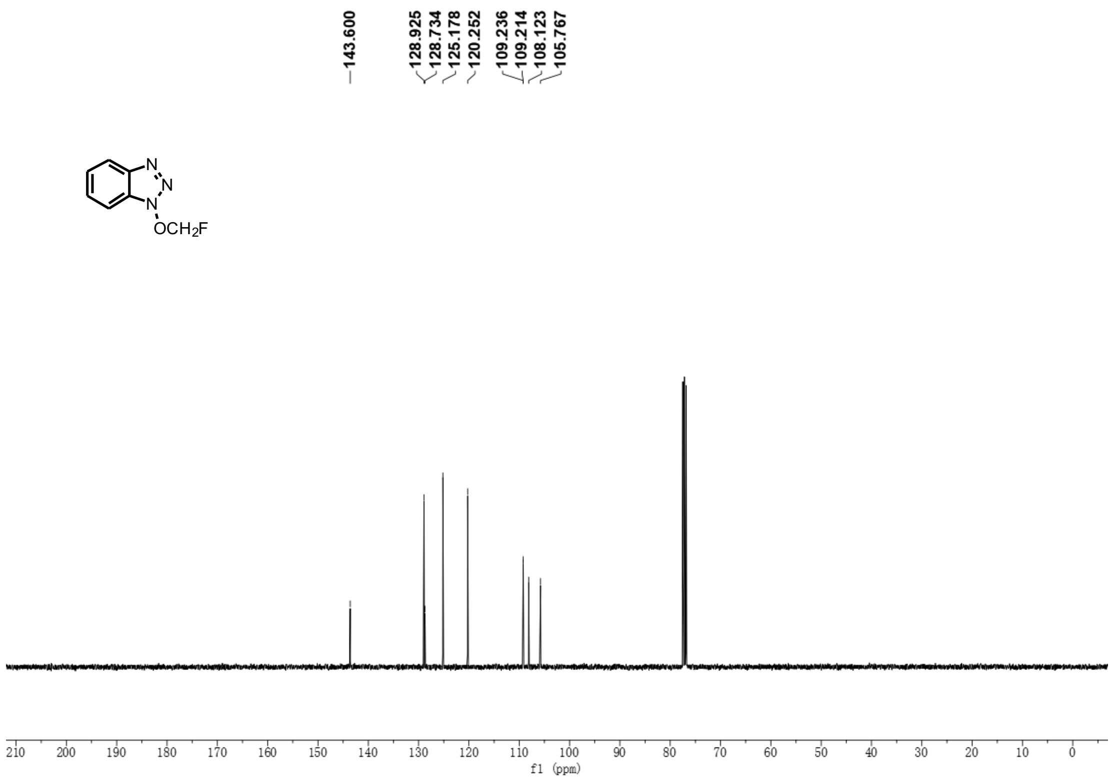
^{19}F NMR Spectrum of Compound **1b** (376 MHz, DMSO-d_6)



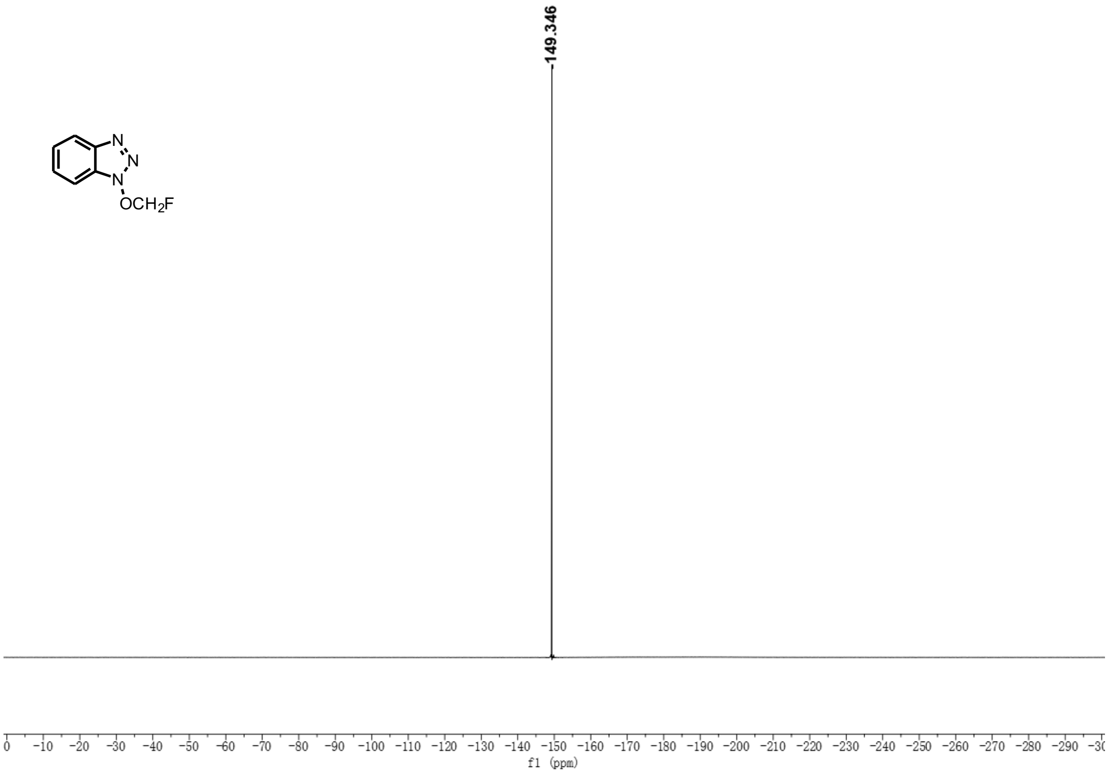
[1]H NMR Spectrum of Compound **S1c** (400 MHz, $CDCl_3$)



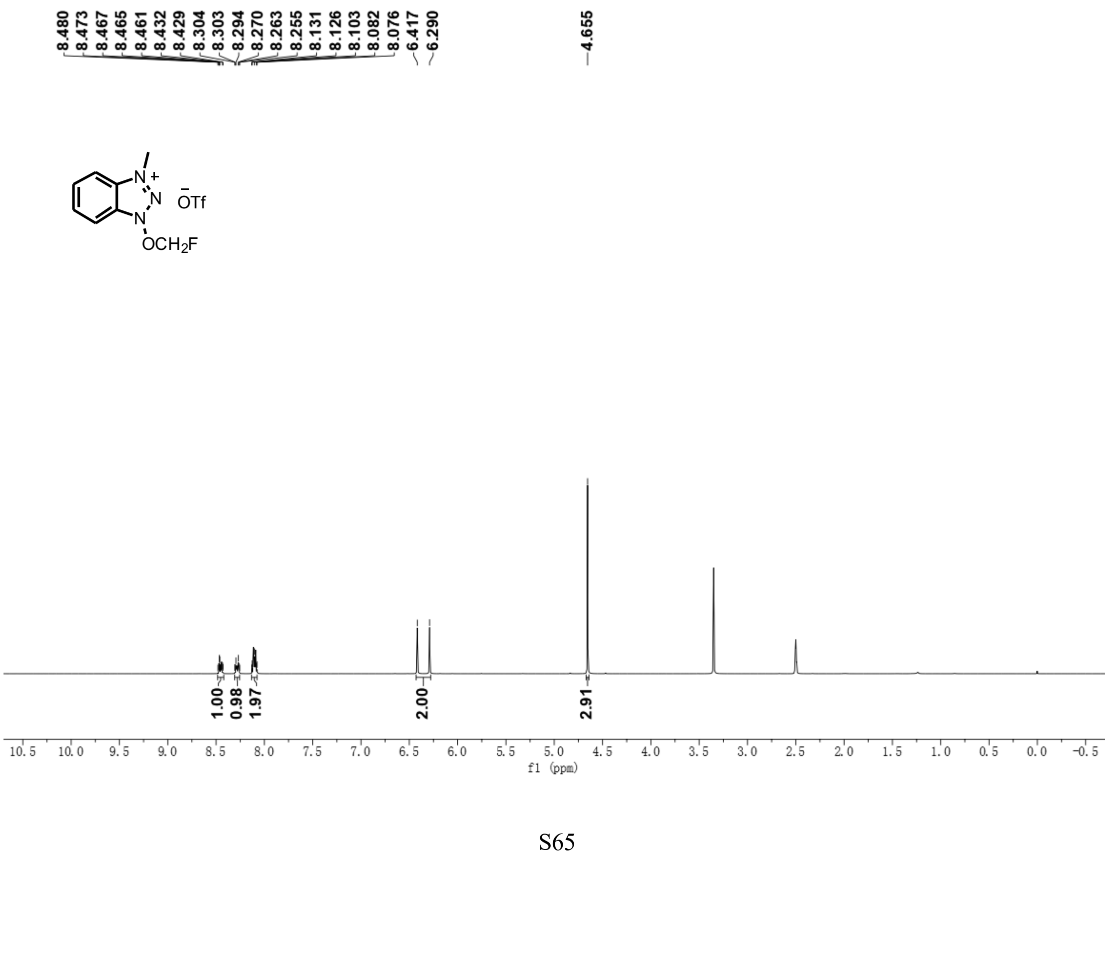
[13]C NMR Spectrum of Compound **S1c** (101 MHz, $CDCl_3$)



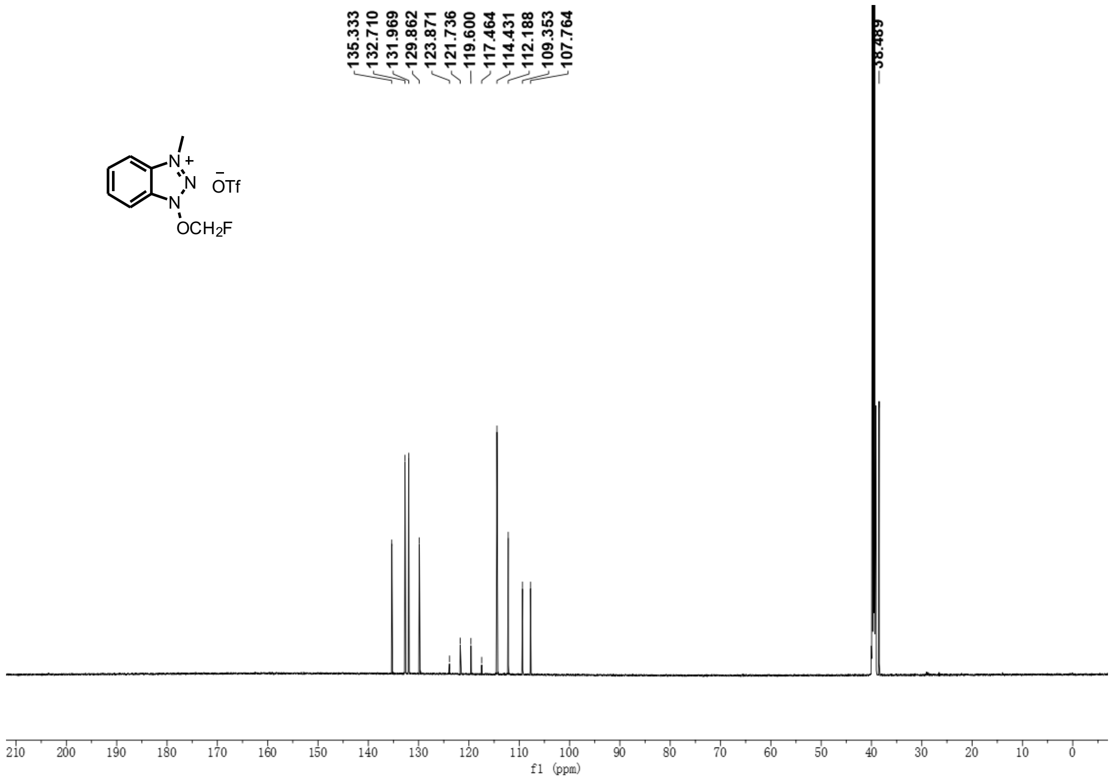
^{19}F NMR Spectrum of Compound **S1c** (376 MHz, DMSO-d_6)



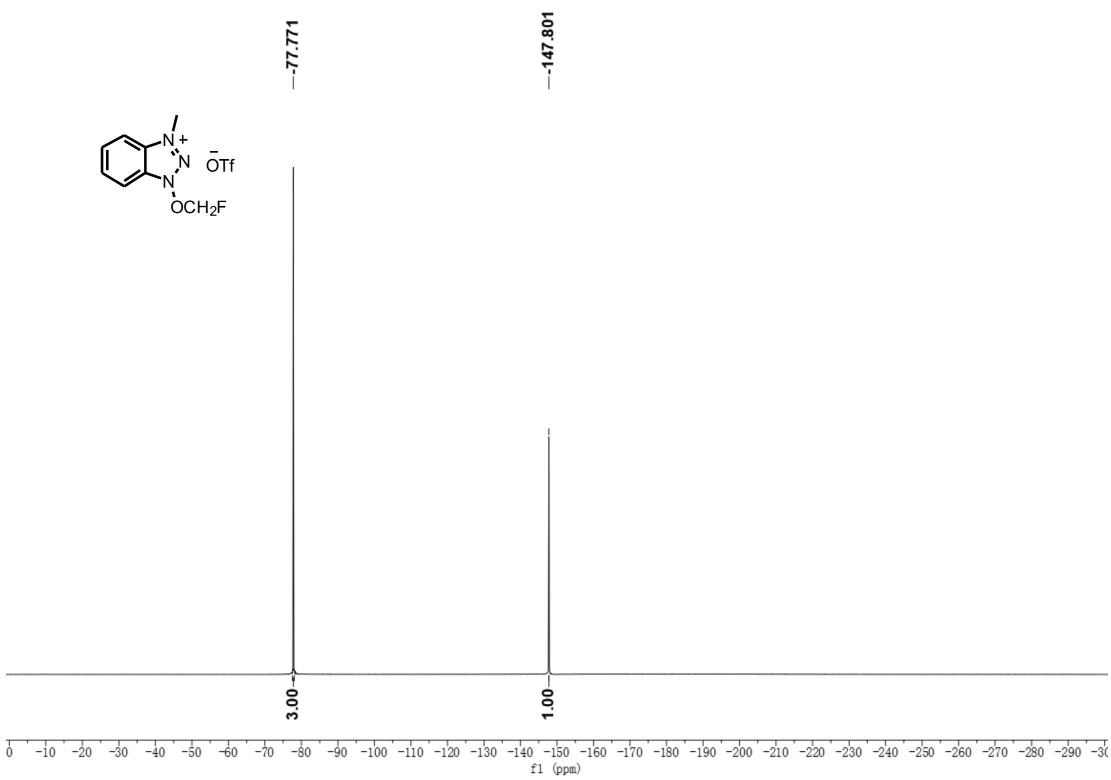
^{1}H NMR Spectrum of Compound **1c** (400 MHz, DMSO-d_6)



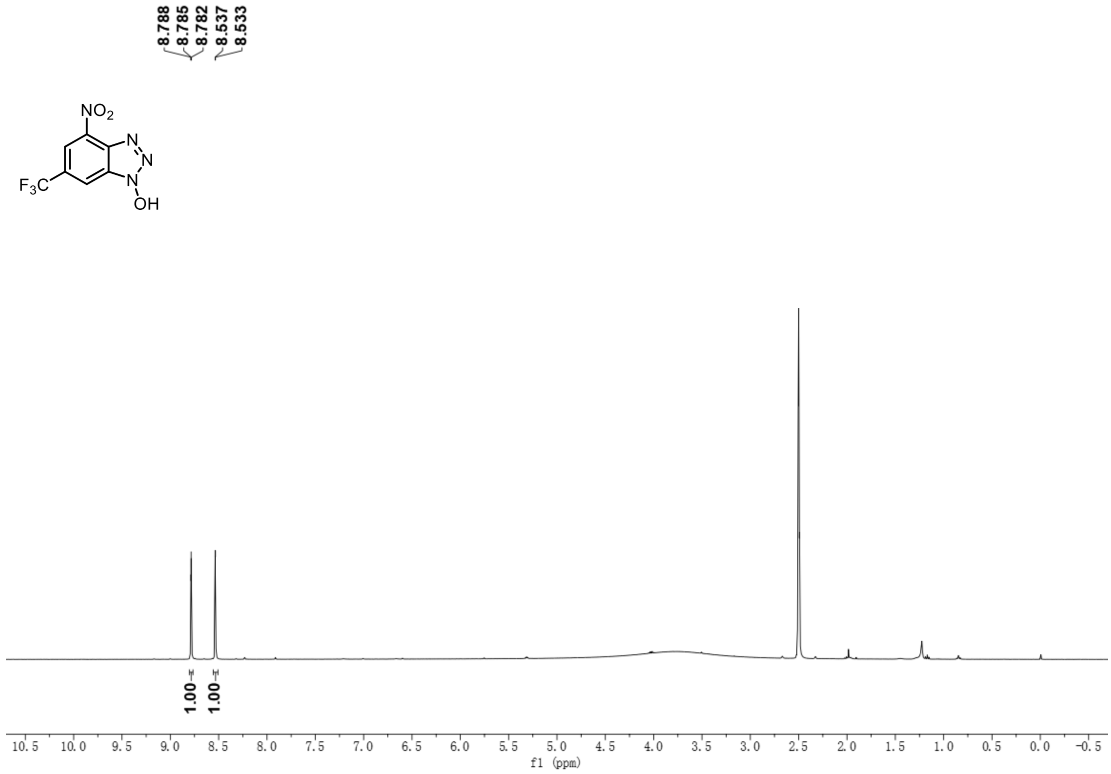
^{13}C NMR Spectrum of Compound **1c** (151 MHz, DMSO-d_6)



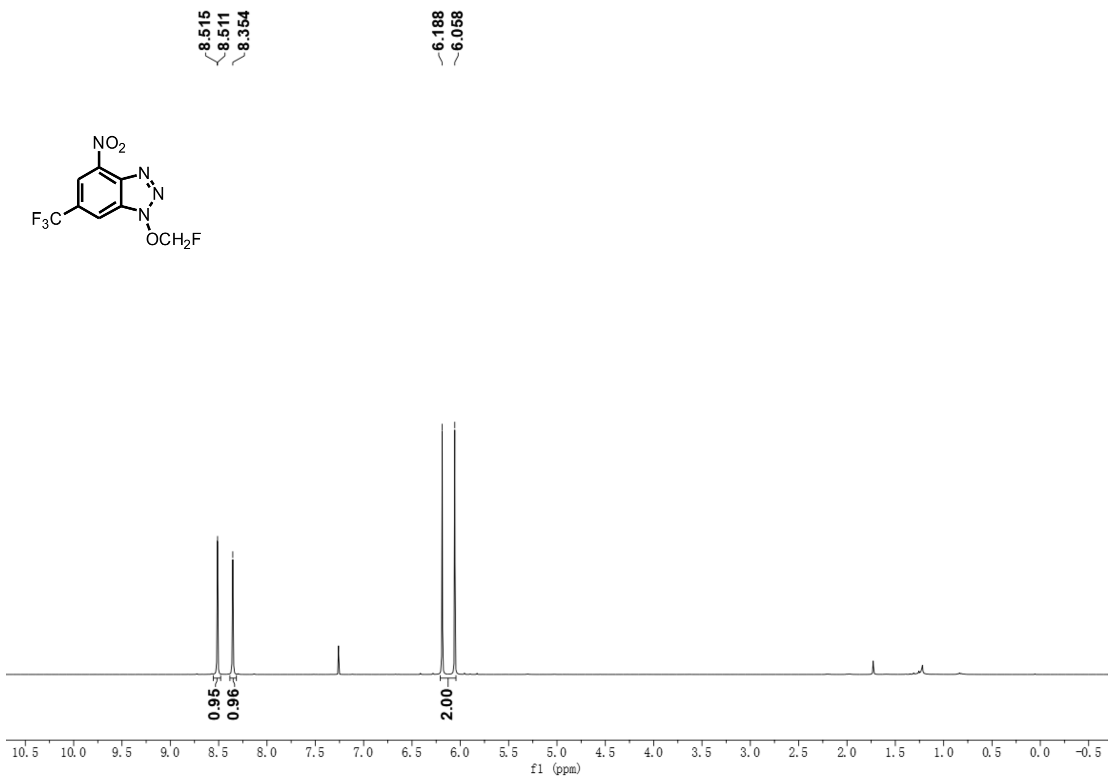
^{19}F NMR Spectrum of Compound **1c** (376 MHz, DMSO-d_6)



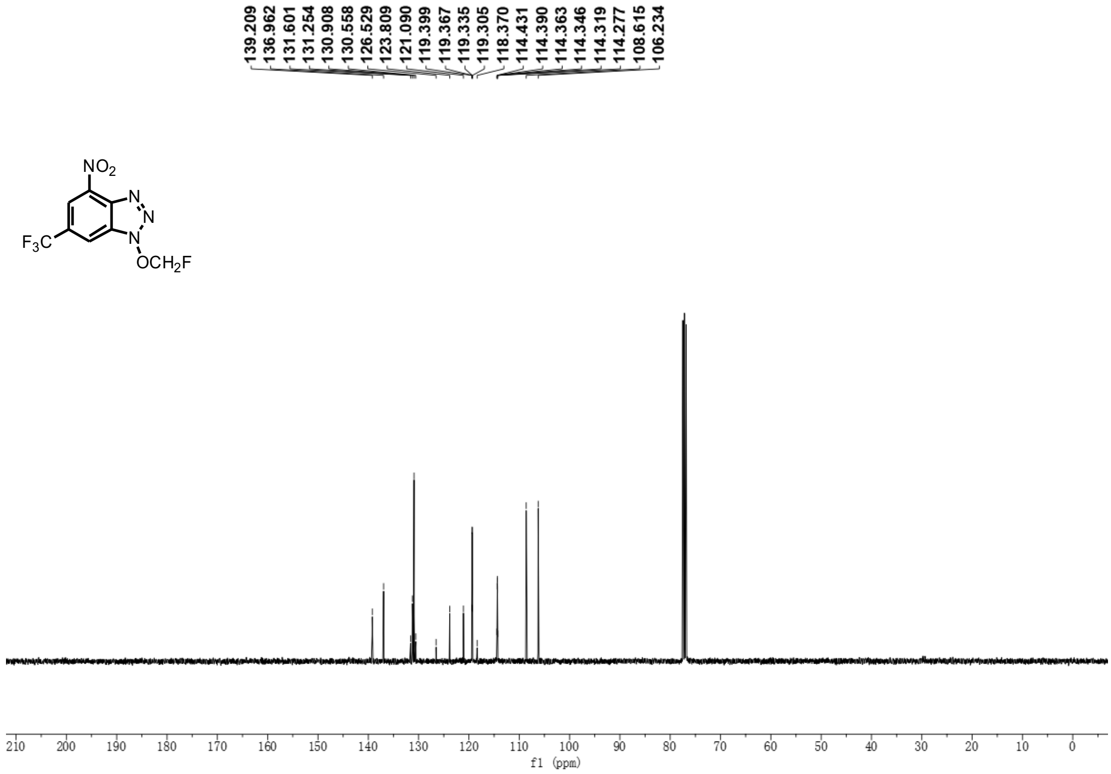
[1]H NMR Spectrum of Compound **S1da** (400 MHz, DMSO-d_6)



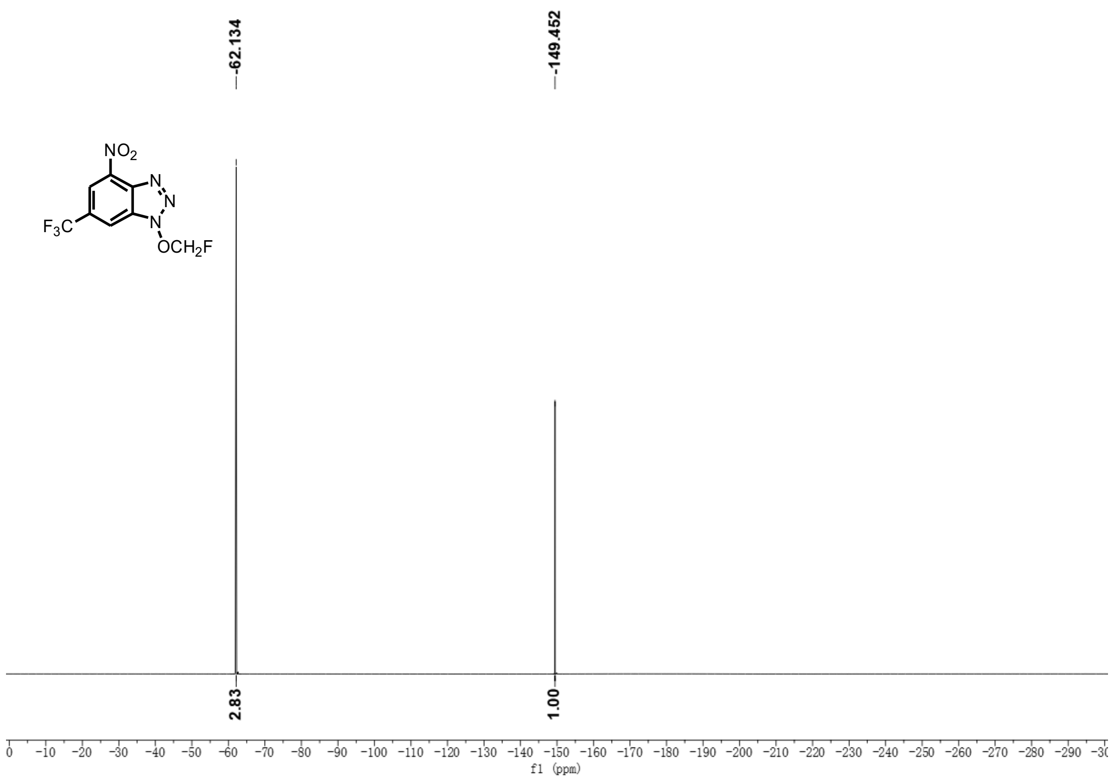
[1]H NMR Spectrum of Compound **S1db** (400 MHz, $CDCl_3$)



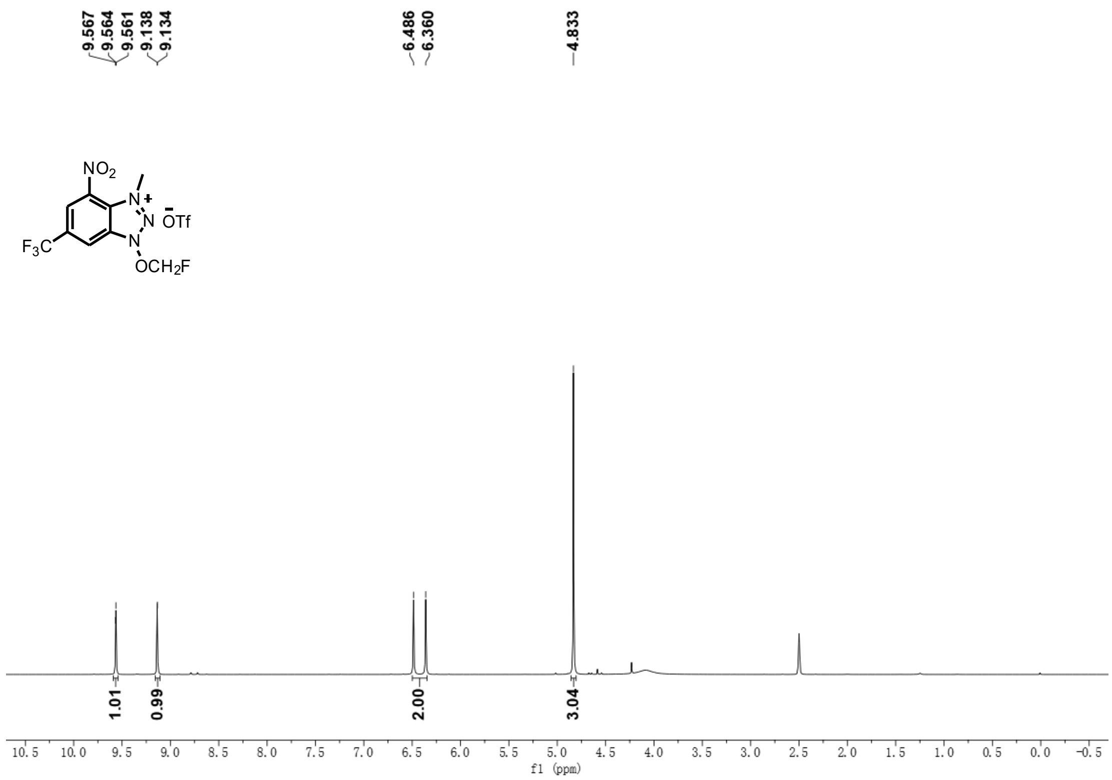
^{13}C NMR Spectrum of Compound **S1db** (101 MHz, $CDCl_3$)



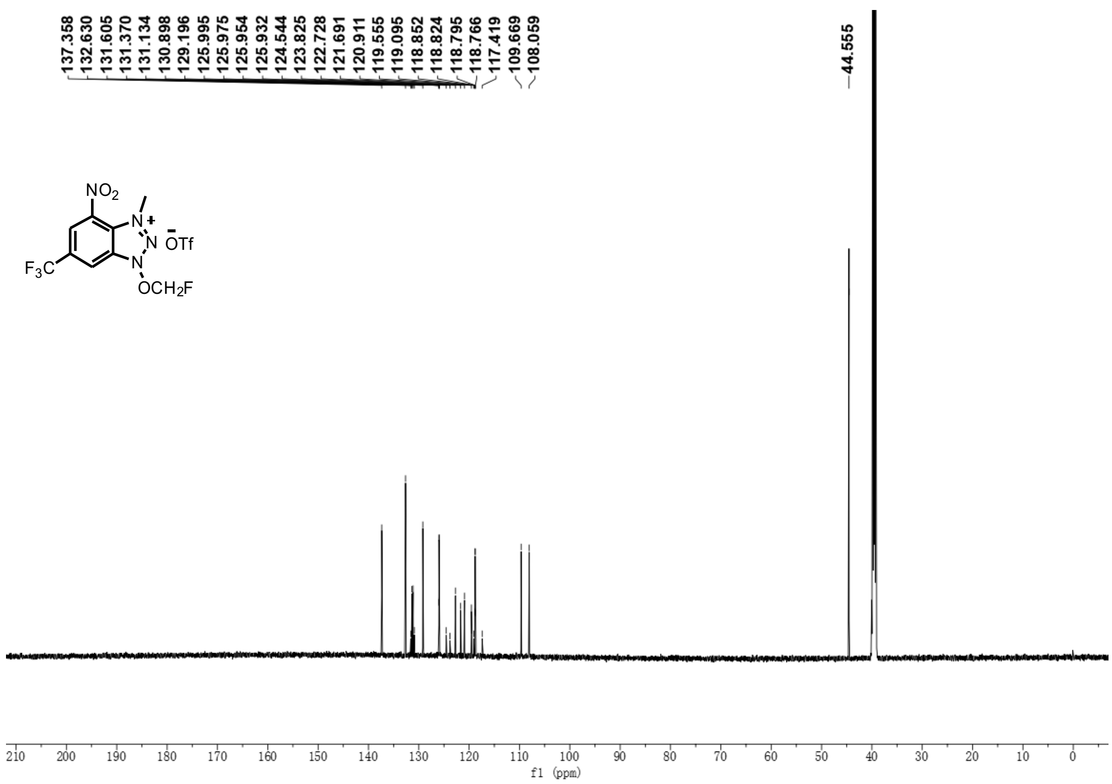
^{19}F NMR Spectrum of Compound **S1db** (376 MHz, $CDCl_3$)



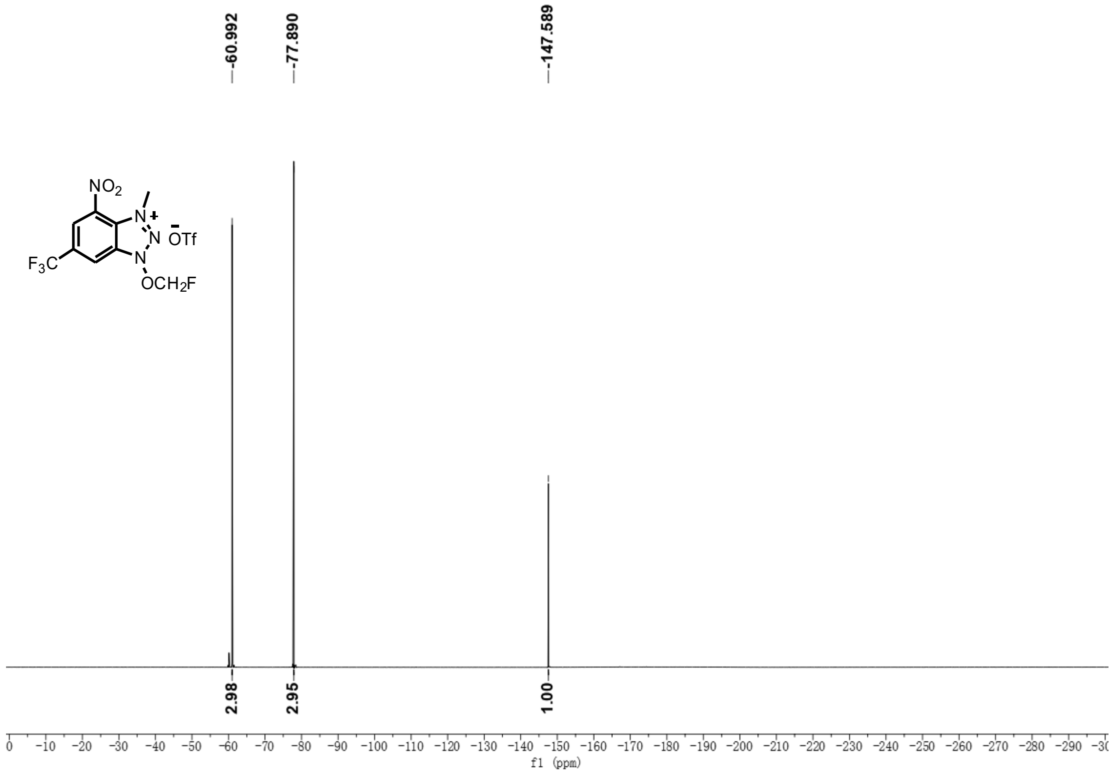
^{1}H NMR Spectrum of Compound **1d** (400 MHz, DMSO-d_6)



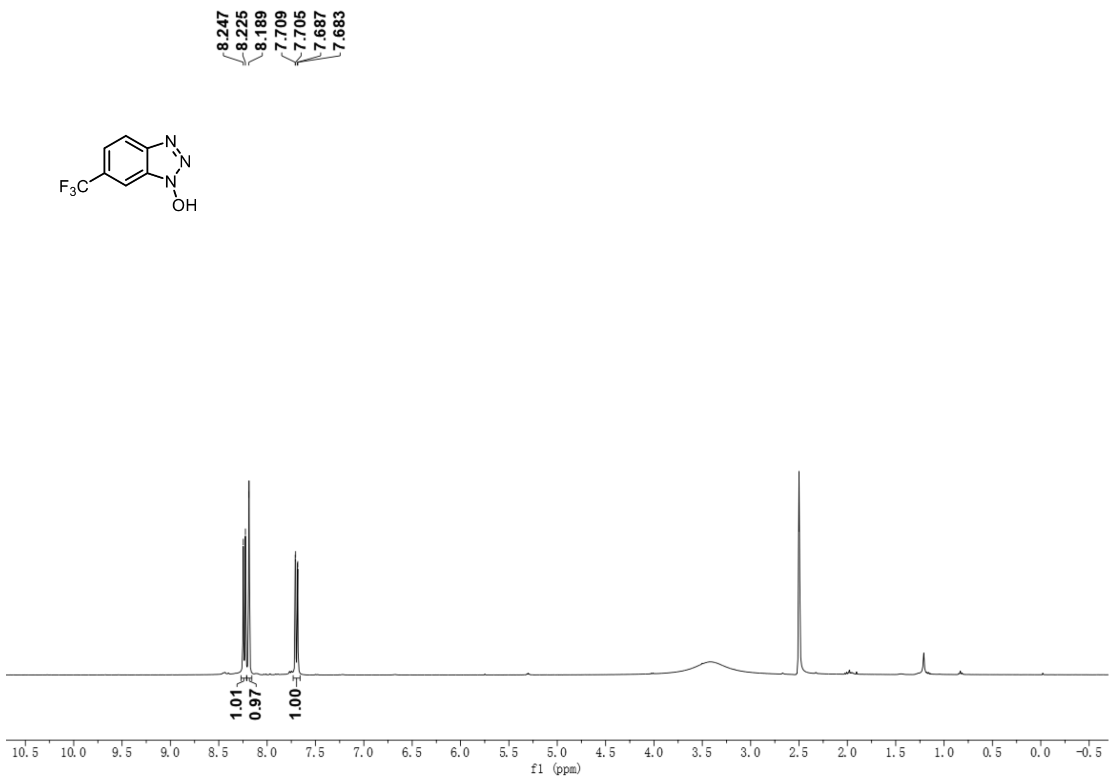
^{13}C NMR Spectrum of Compound **1d** (151 MHz, DMSO-d_6)



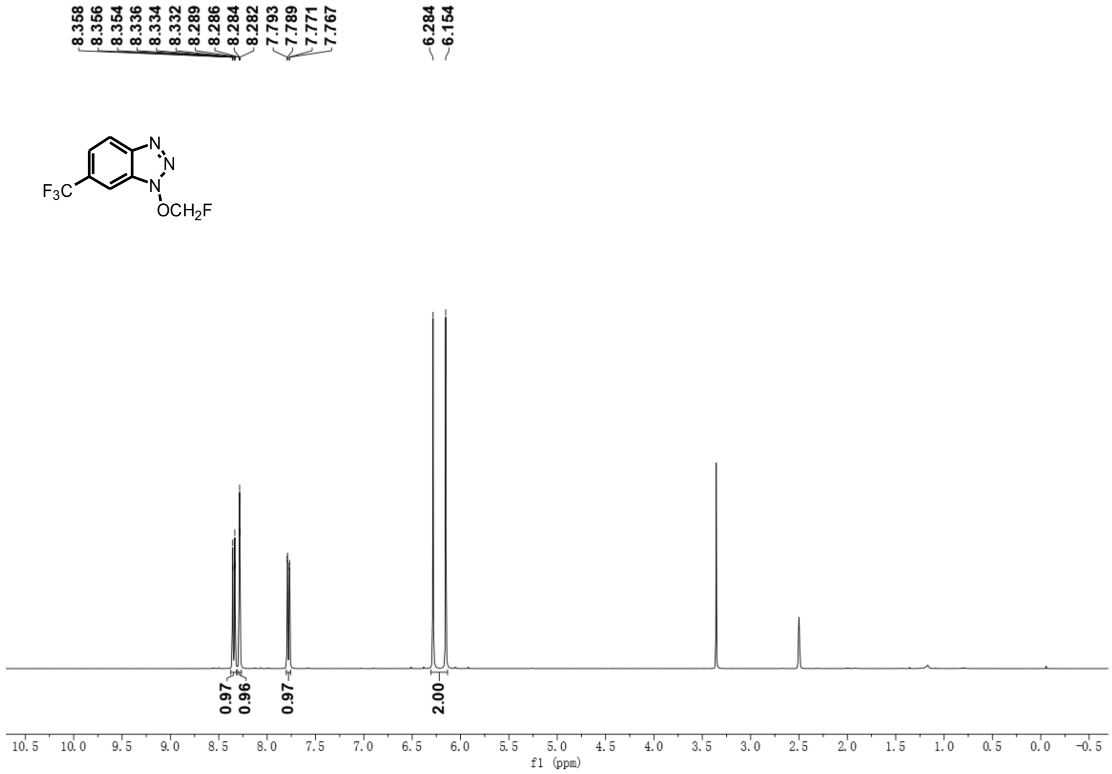
^{19}F NMR Spectrum of Compound **1d** (376 MHz, DMSO-d_6)



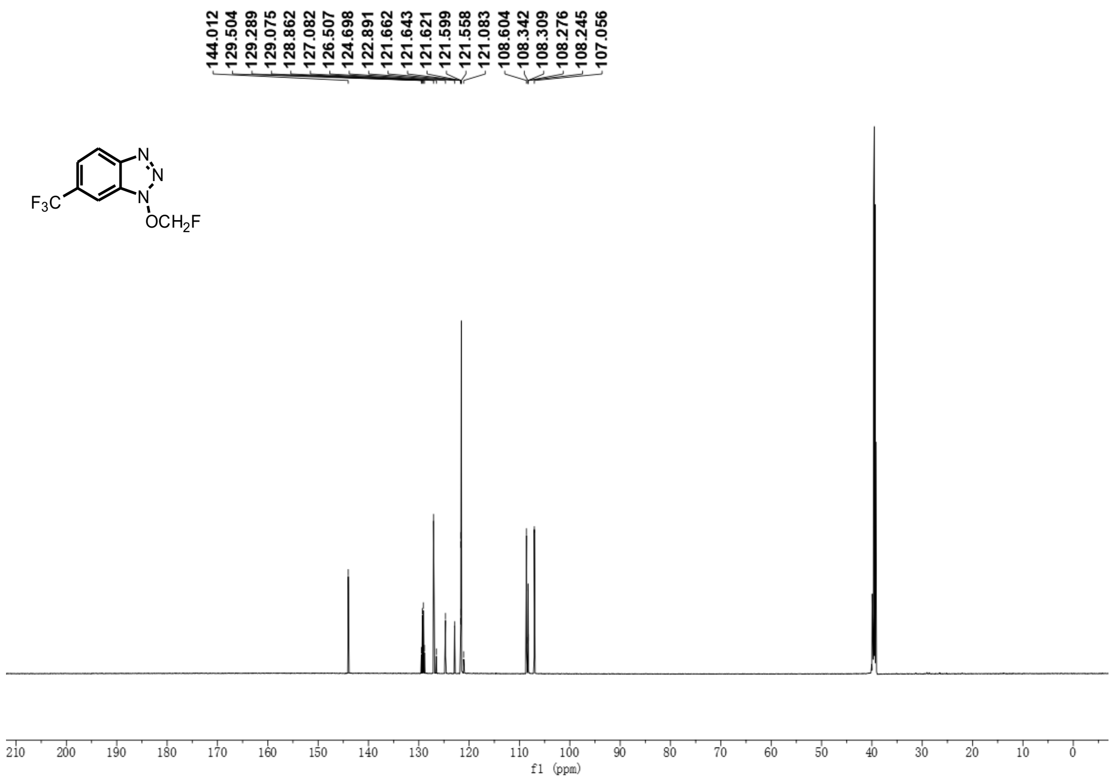
^{1}H NMR Spectrum of Compound **S1ea** (400 MHz, DMSO-d_6)



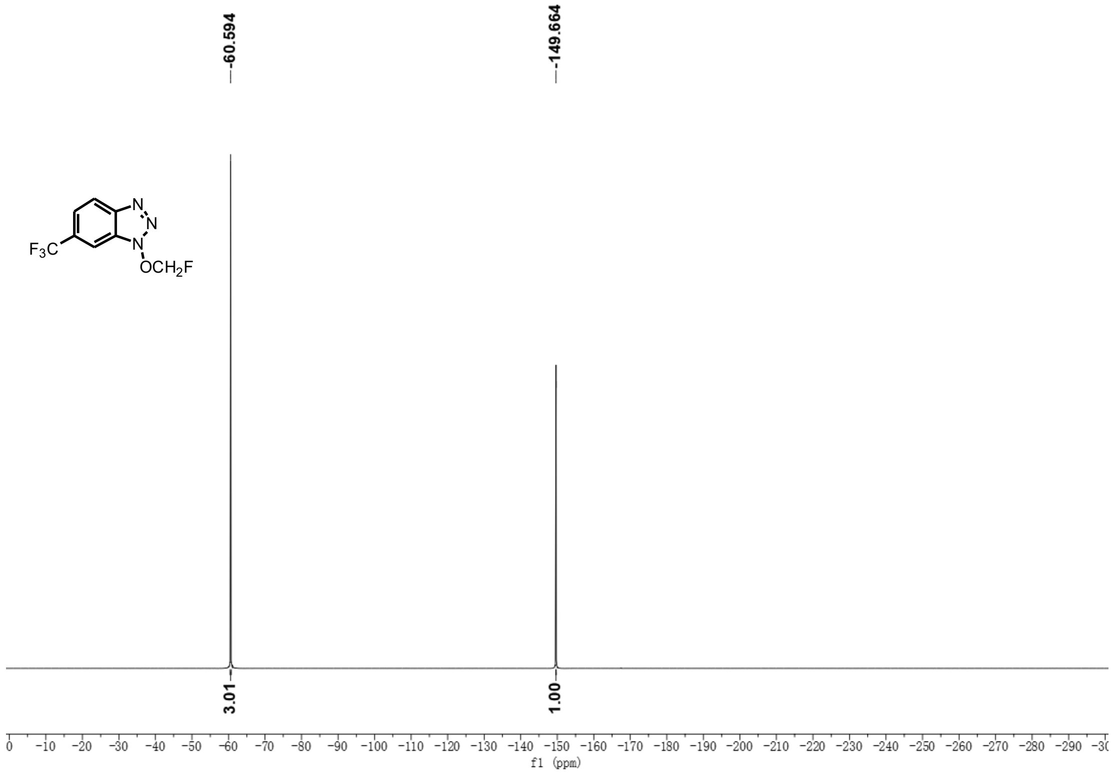
^{1}H NMR Spectrum of Compound **S1eb** (400 MHz, DMSO-d_6)



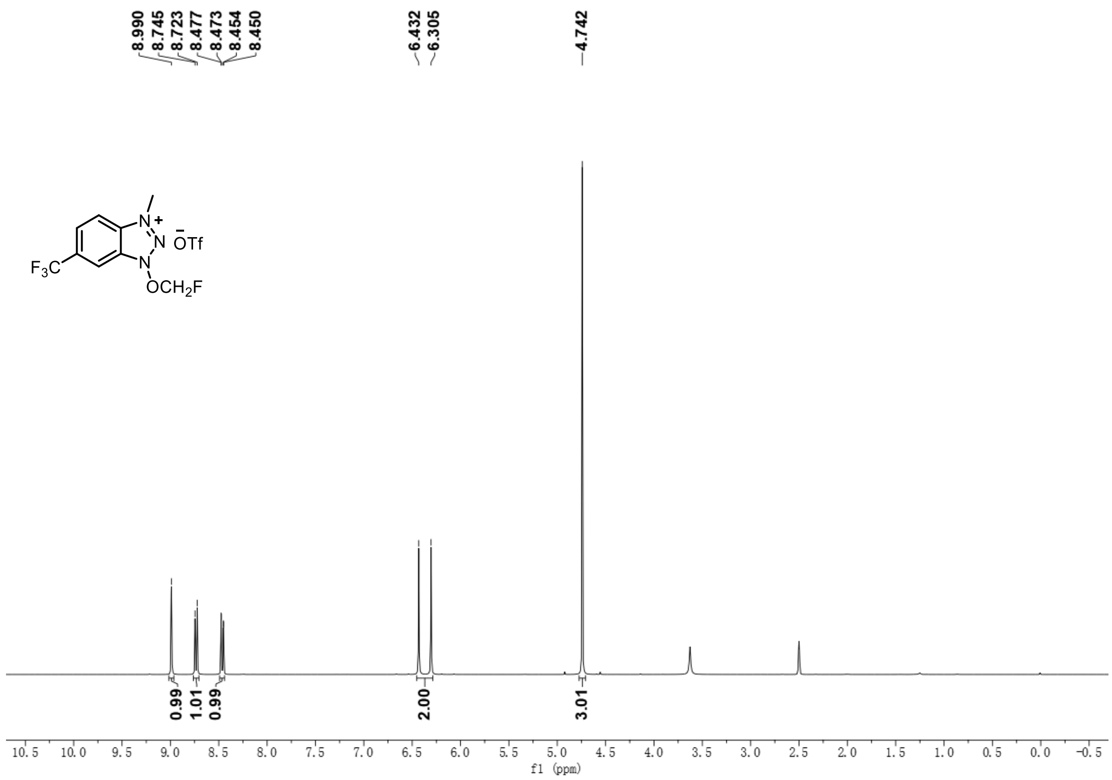
^{13}C NMR Spectrum of Compound **S1eb** (101 MHz, DMSO-d_6)



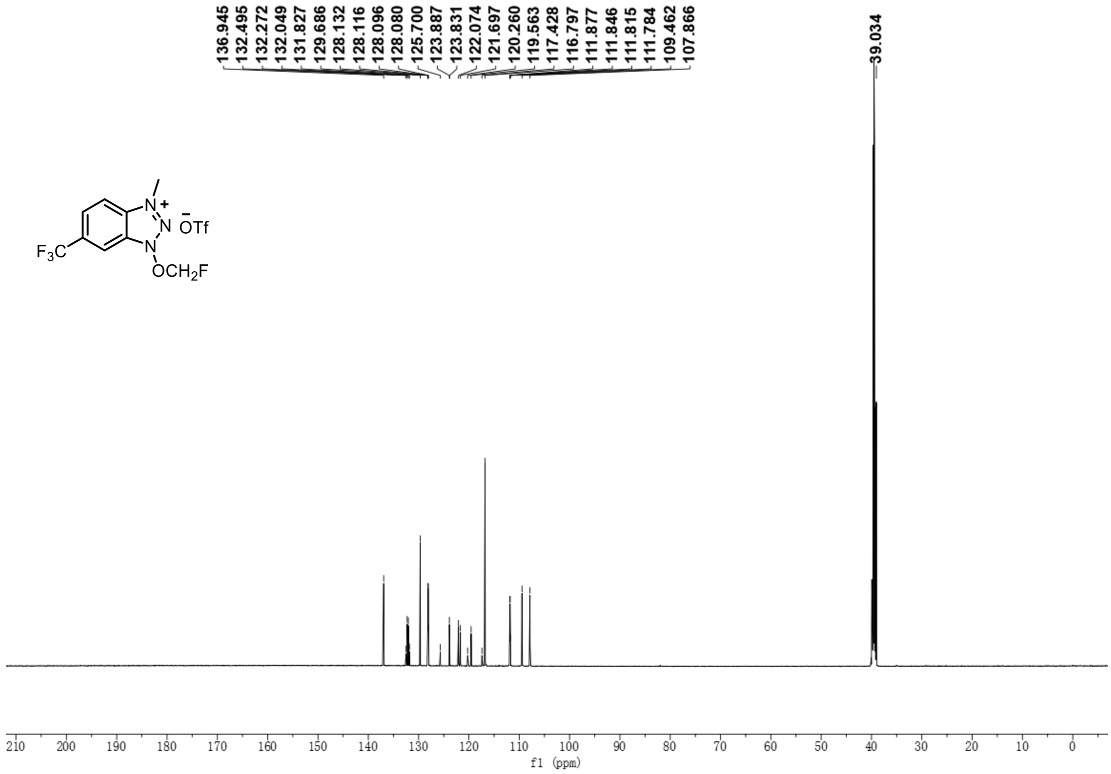
^{19}F NMR Spectrum of Compound **S1eb** (376 MHz, DMSO-d_6)



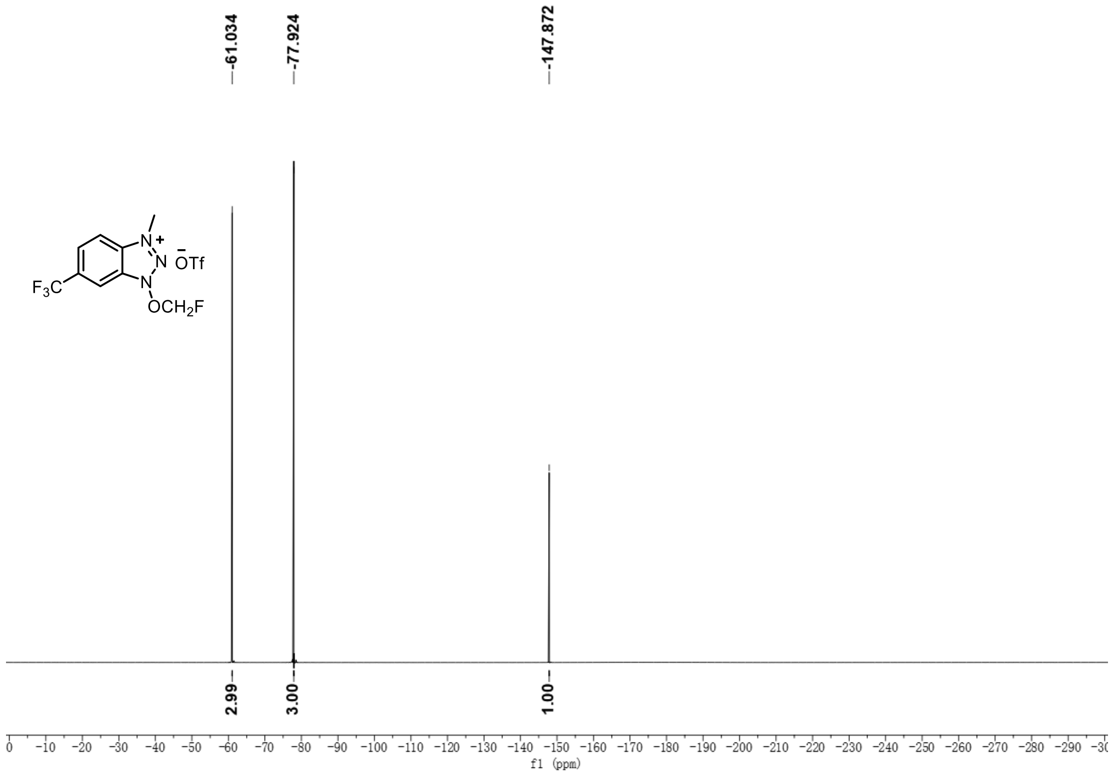
^{1}H NMR Spectrum of Compound **1e** (400 MHz, DMSO-d_6)



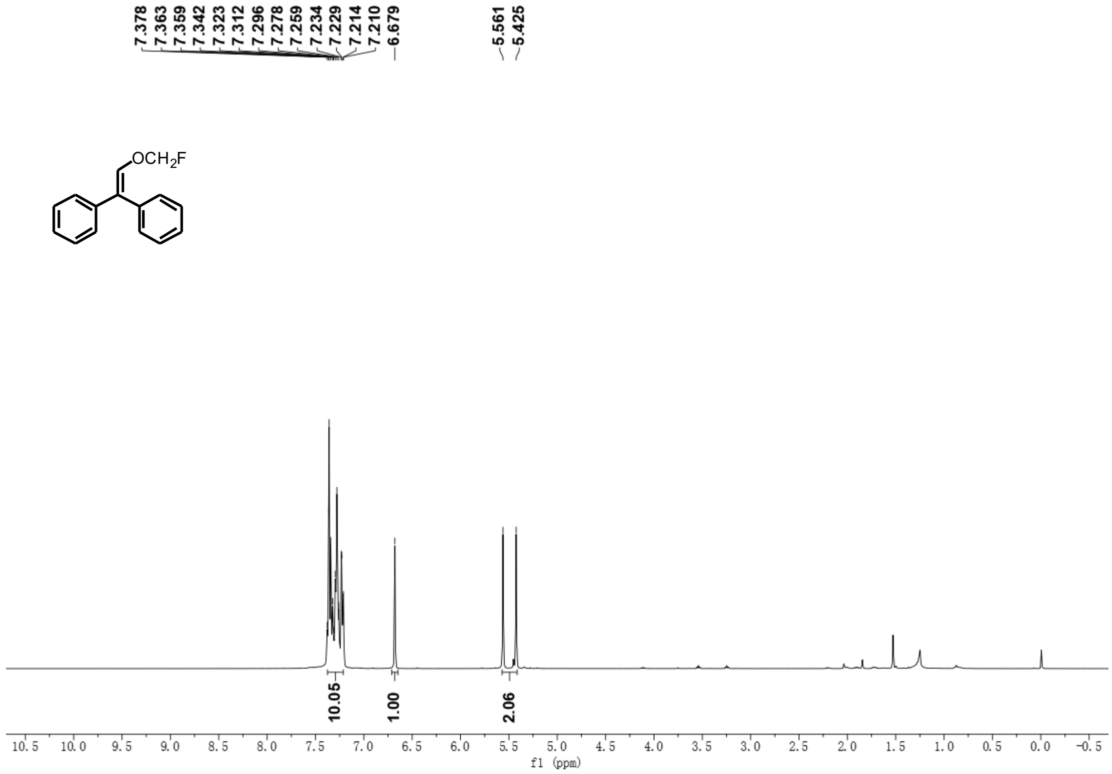
^{13}C NMR Spectrum of Compound **1e** (151 MHz, DMSO-d_6)



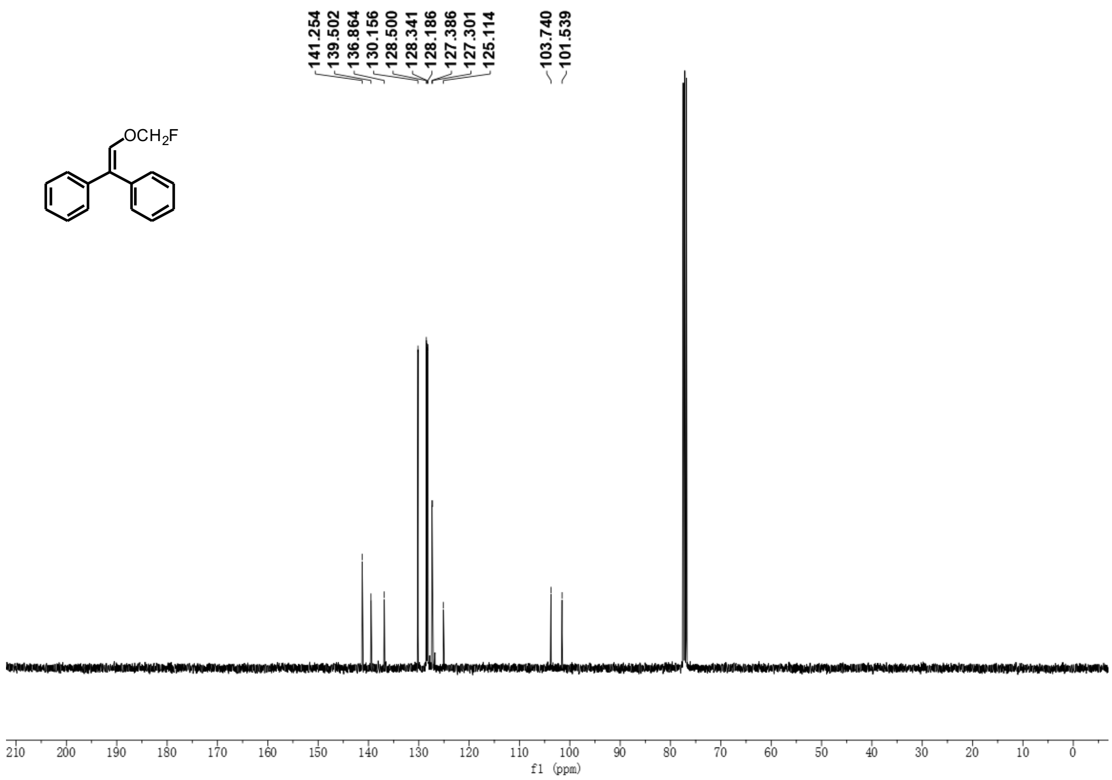
^{19}F NMR Spectrum of Compound **1e** (376 MHz, DMSO-d_6)



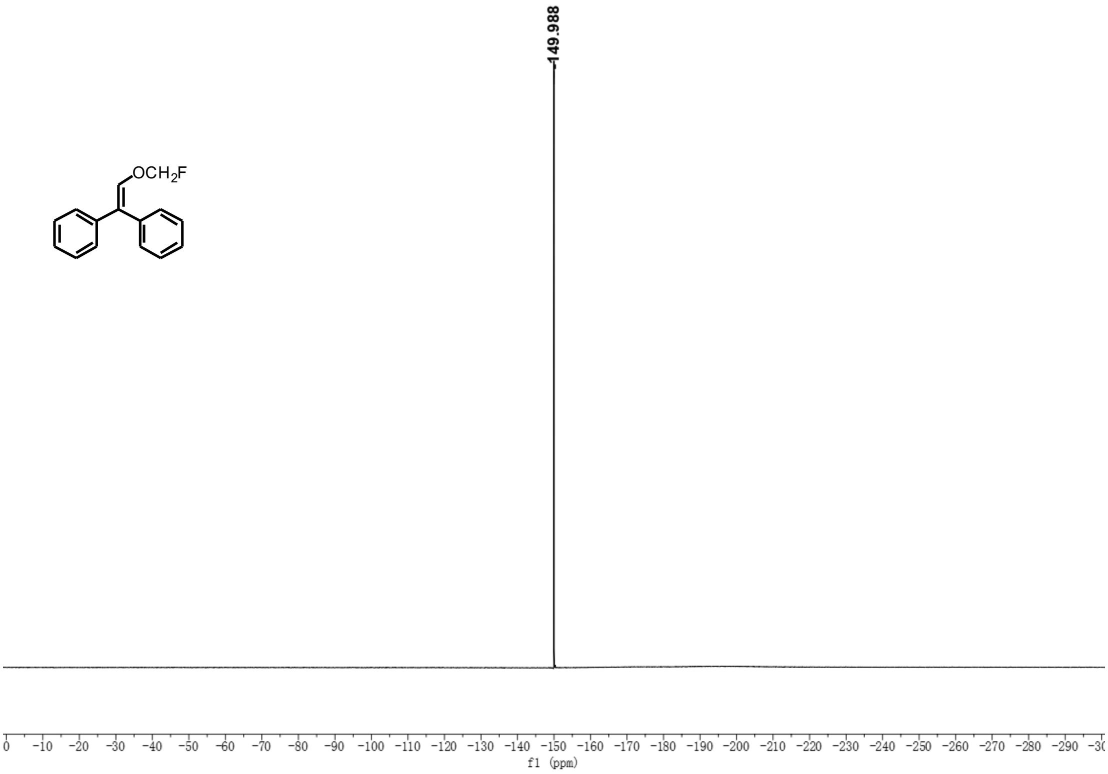
^{1}H NMR Spectrum of Compound **3** (400 MHz, $CDCl_3$)



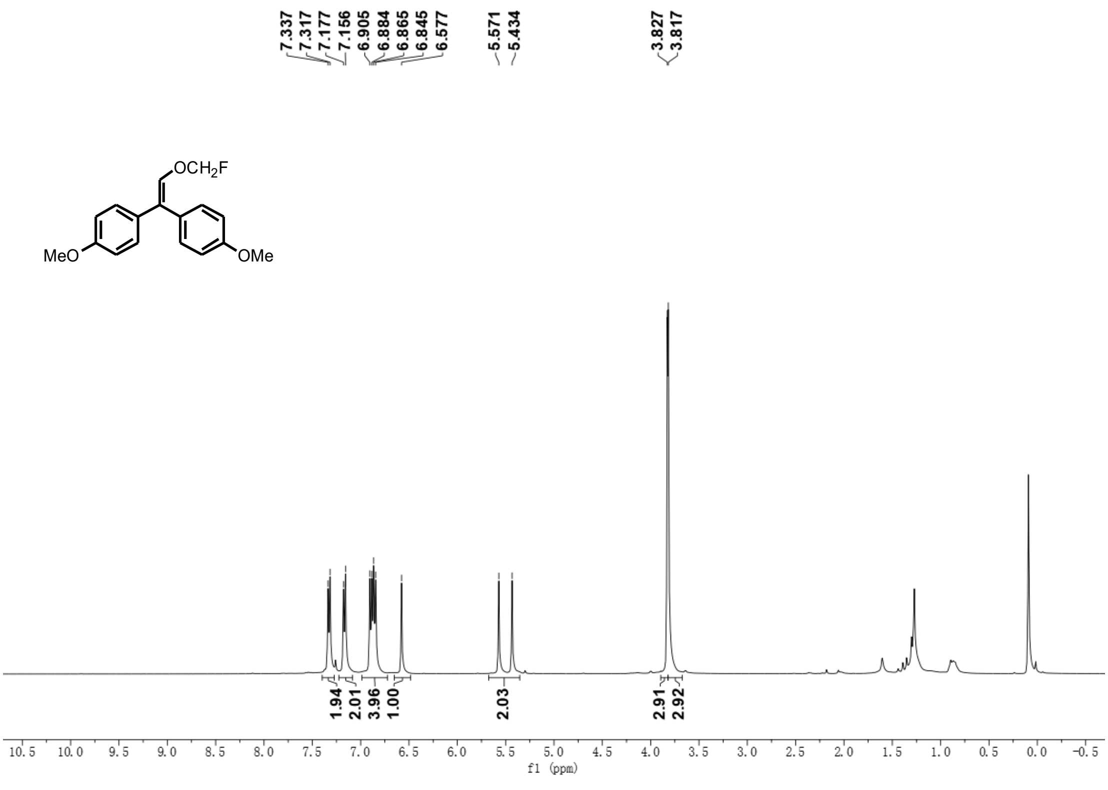
^{13}C NMR Spectrum of Compound **3** (400 MHz, $CDCl_3$)



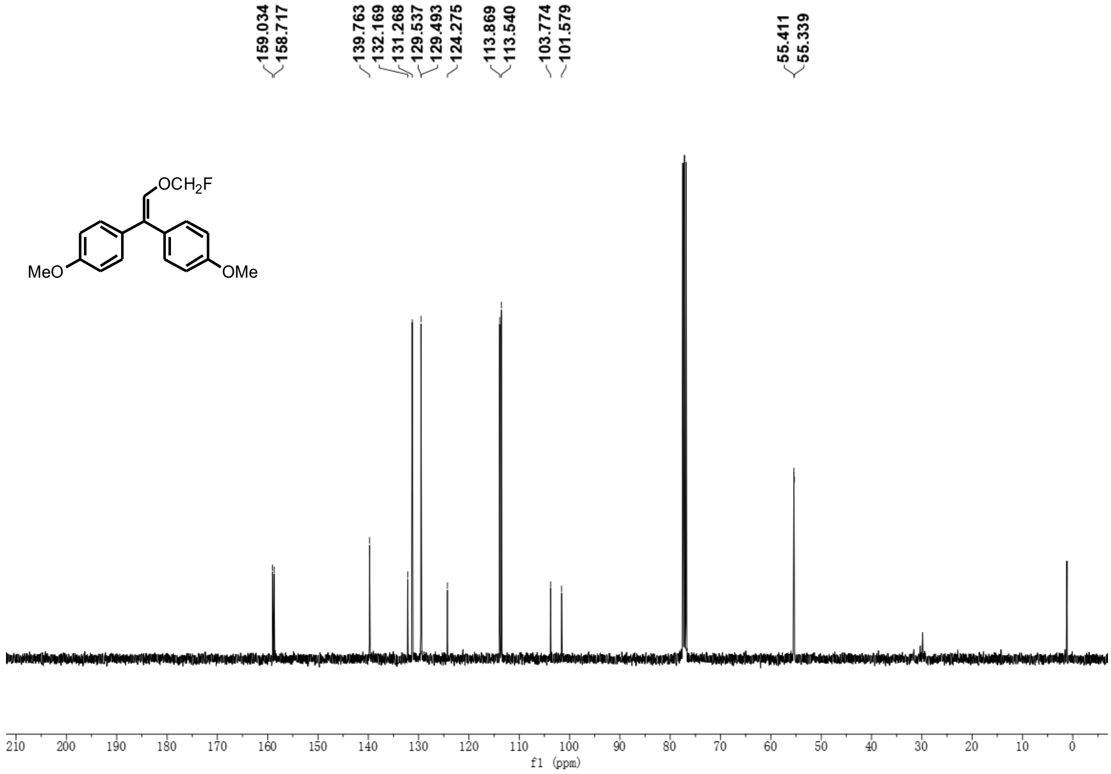
^{19}F NMR Spectrum of Compound **3** (376 MHz, $CDCl_3$)



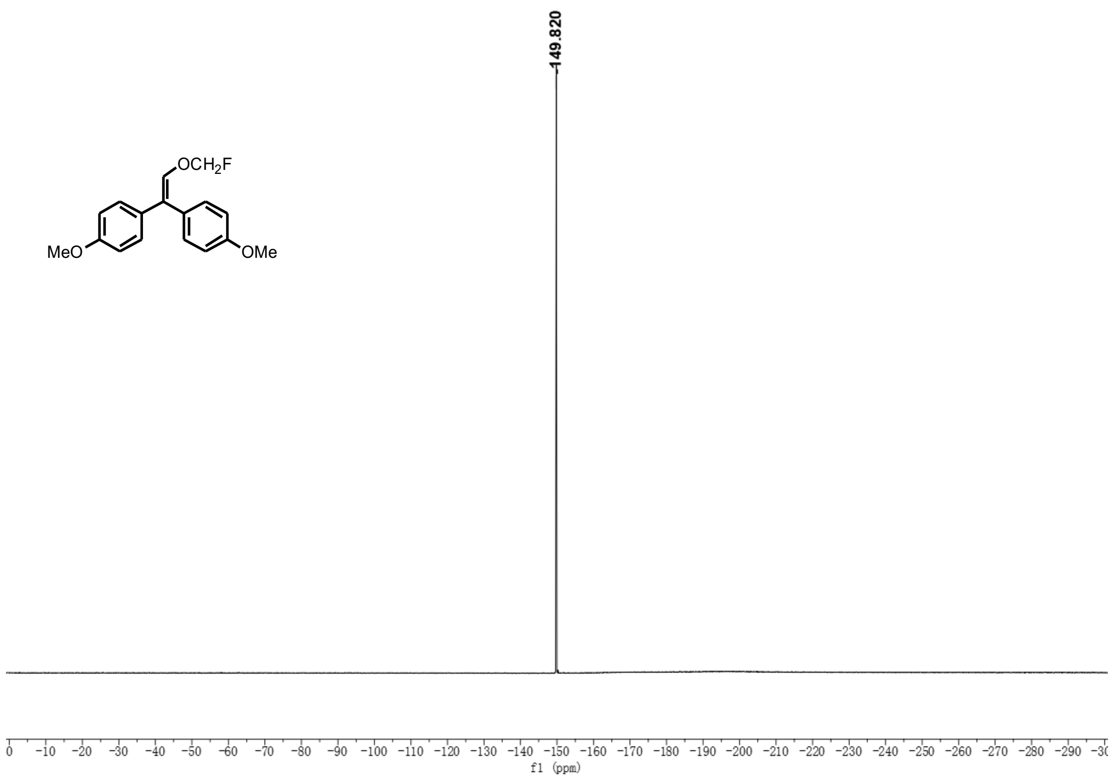
^{1}H NMR Spectrum of Compound **4** (400 MHz, $CDCl_3$)



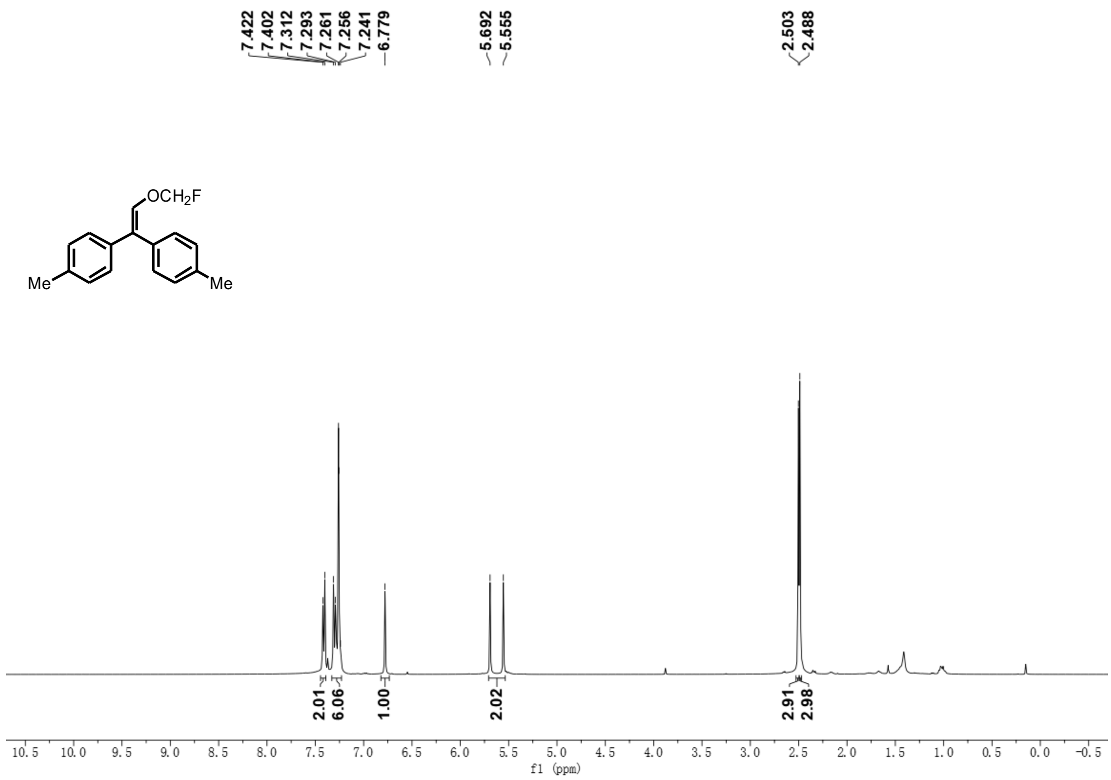
^{13}C NMR Spectrum of Compound **4** (400 MHz, $CDCl_3$)



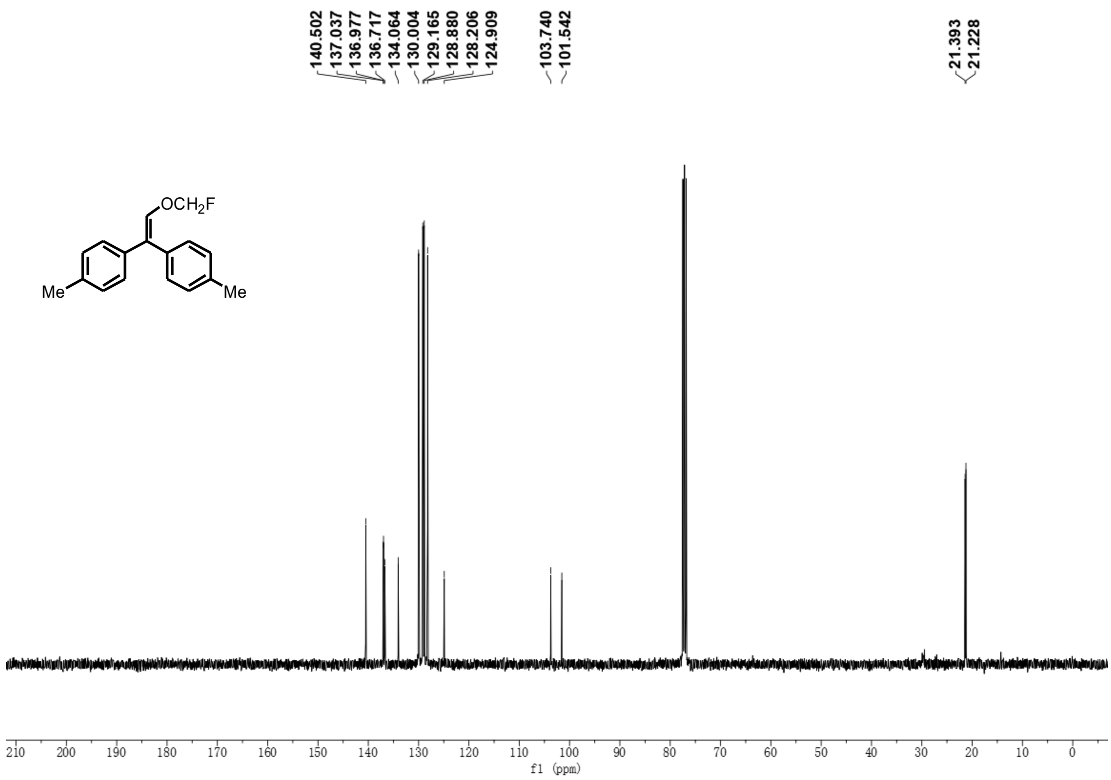
^{19}F NMR Spectrum of Compound **4** (376 MHz, $CDCl_3$)



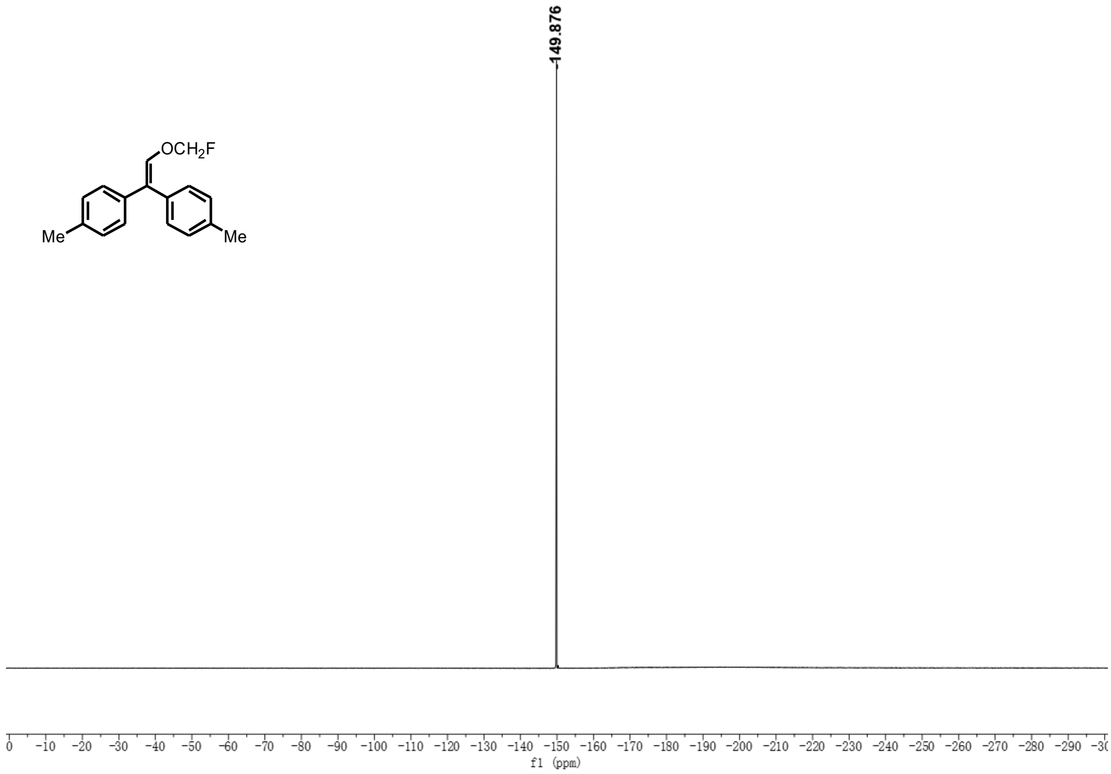
^{1}H NMR Spectrum of Compound **5** (400 MHz, $CDCl_3$)



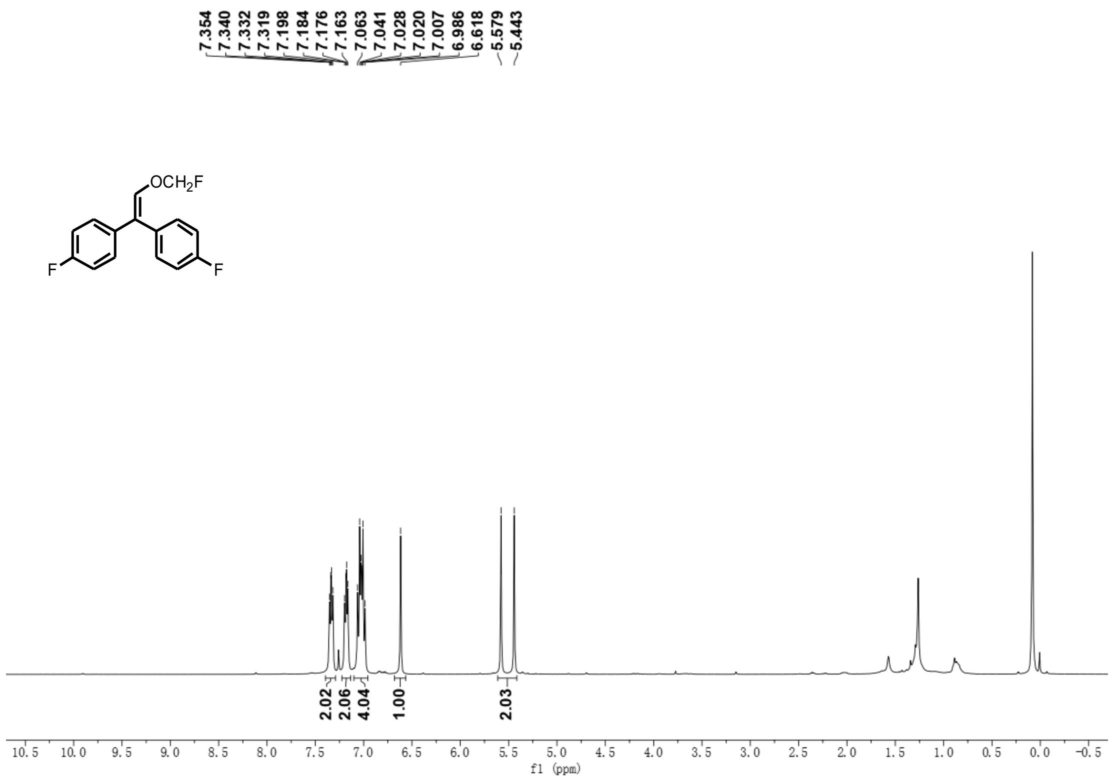
^{13}C NMR Spectrum of Compound **5** (400 MHz, $CDCl_3$)



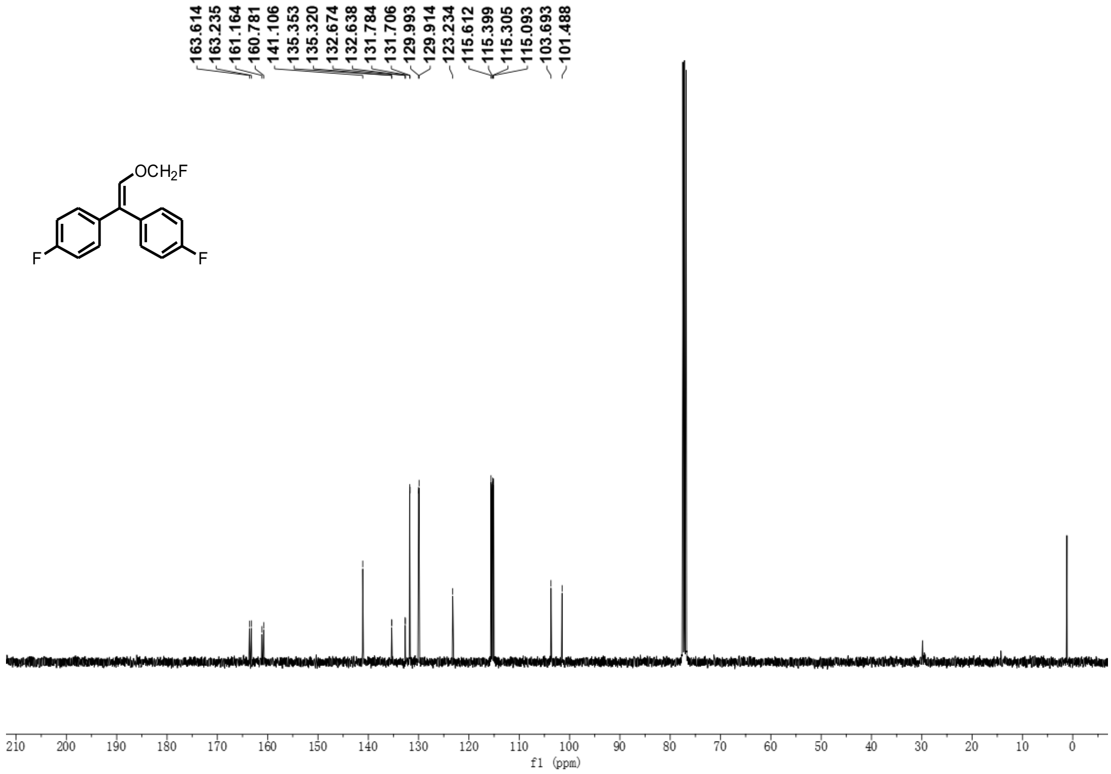
^{19}F NMR Spectrum of Compound **5** (376 MHz, $CDCl_3$)



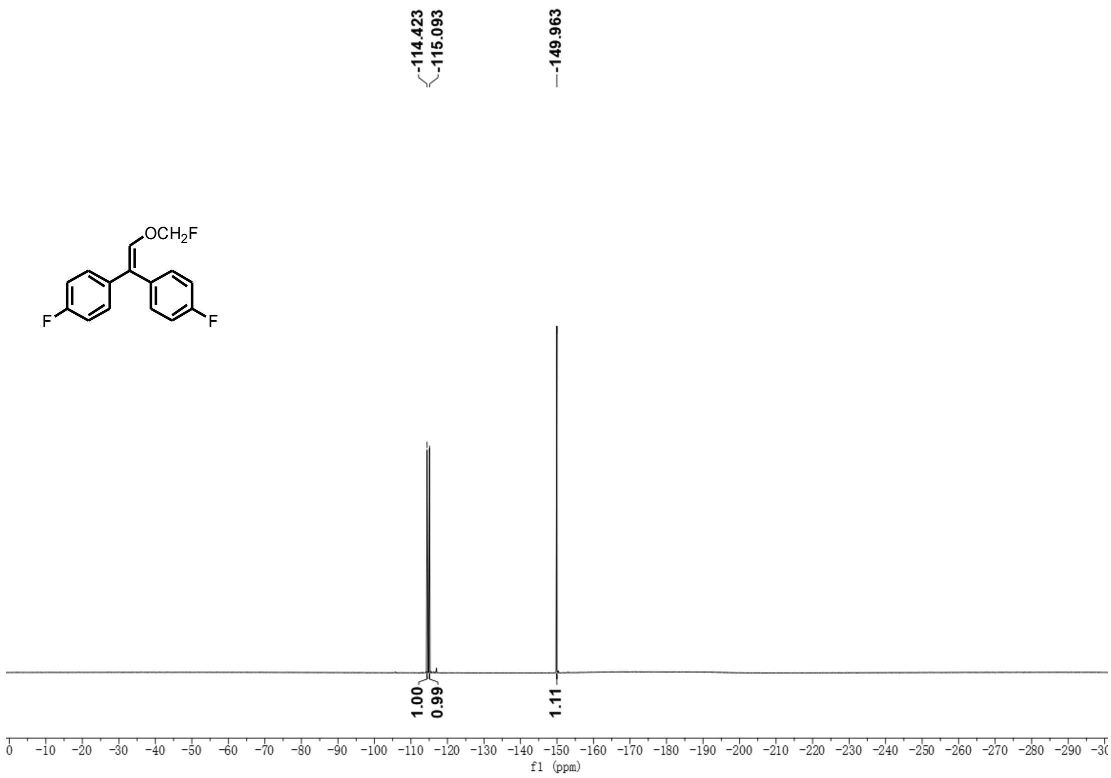
^{1}H NMR Spectrum of Compound **6** (400 MHz, $CDCl_3$)



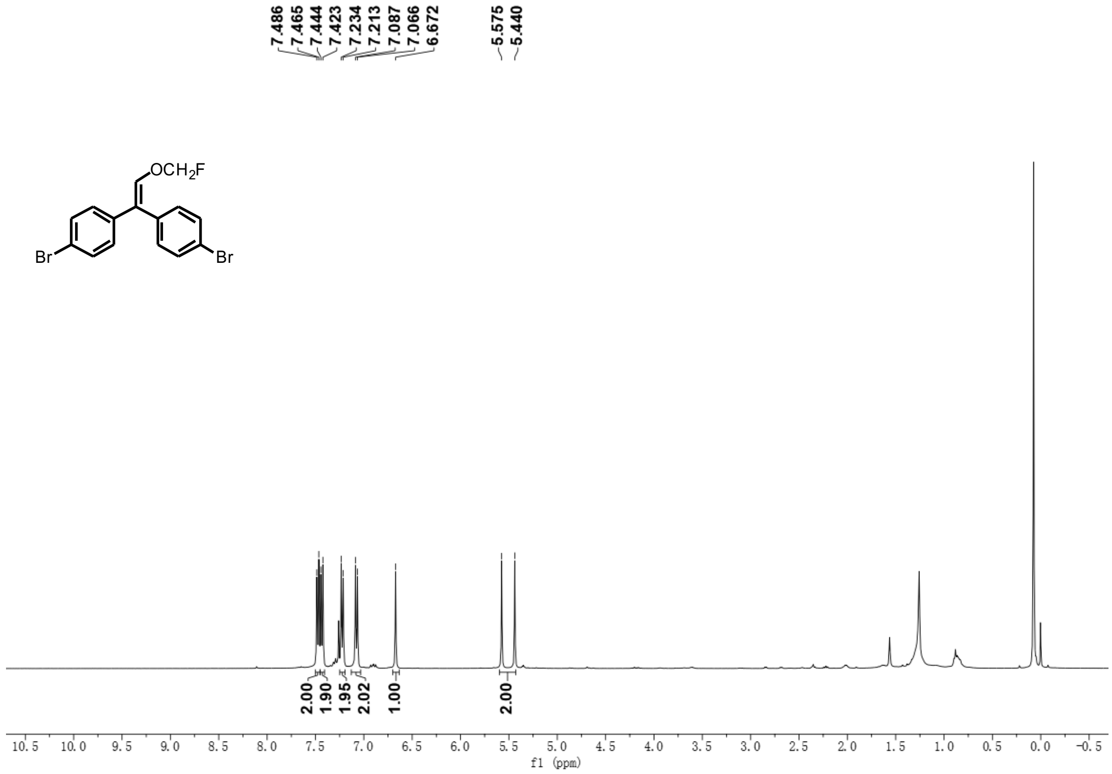
^{13}C NMR Spectrum of Compound **6** (101 MHz, $CDCl_3$)



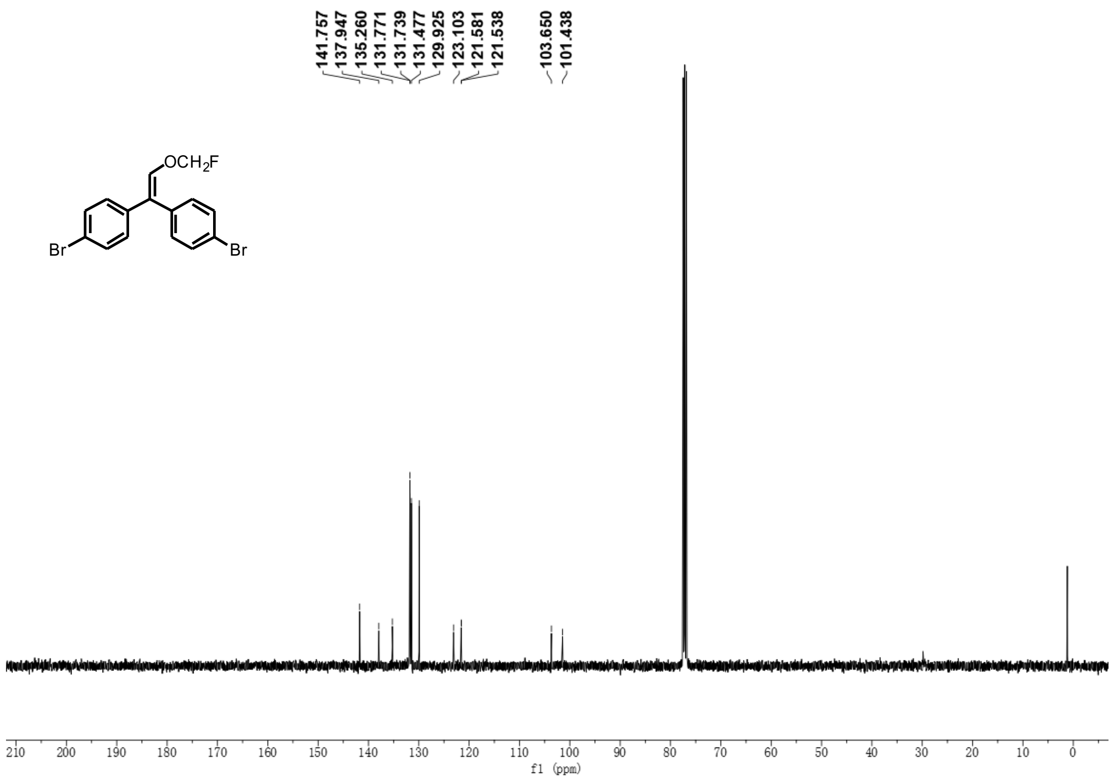
^{19}F NMR Spectrum of Compound **6** (376 MHz, $CDCl_3$)



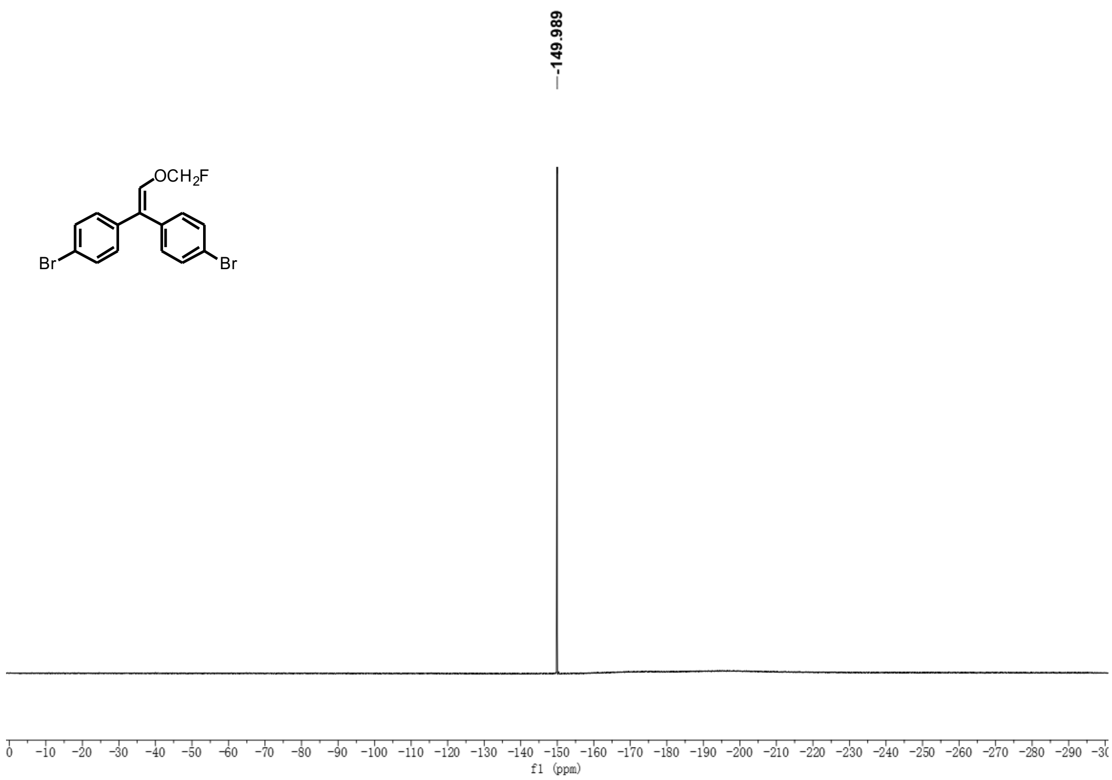
^{1}H NMR Spectrum of Compound **7** (400 MHz, $CDCl_3$)



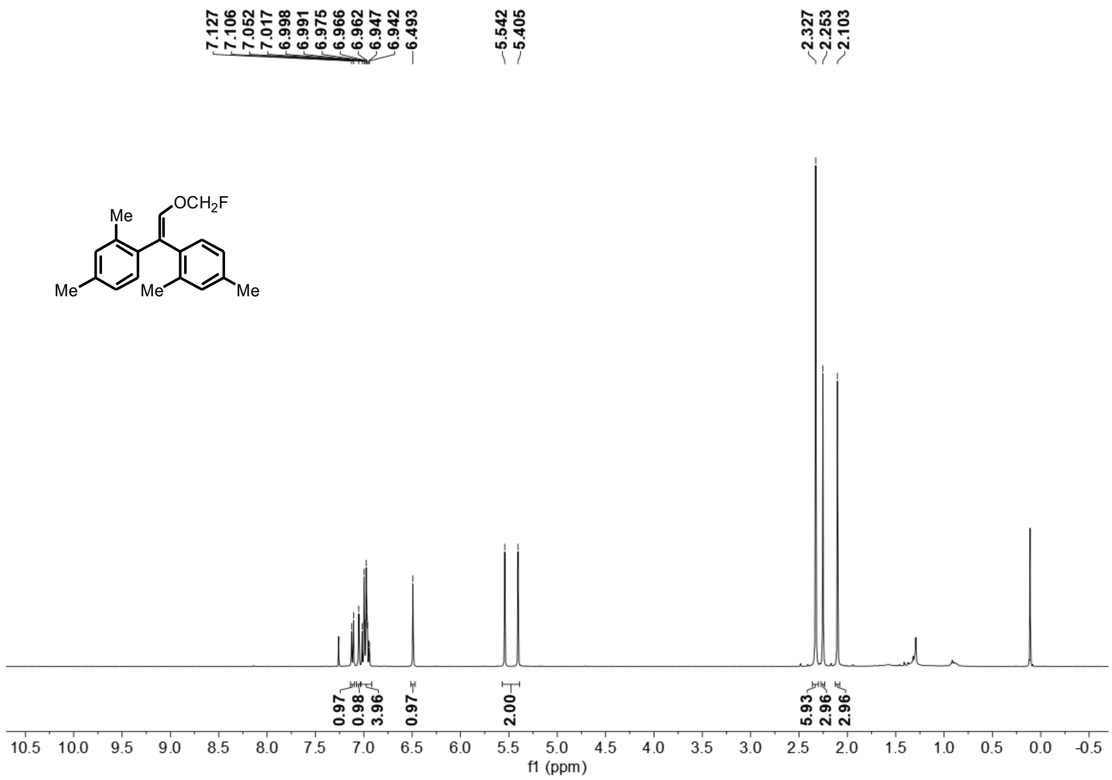
^{13}C NMR Spectrum of Compound **7** (101 MHz, $CDCl_3$)



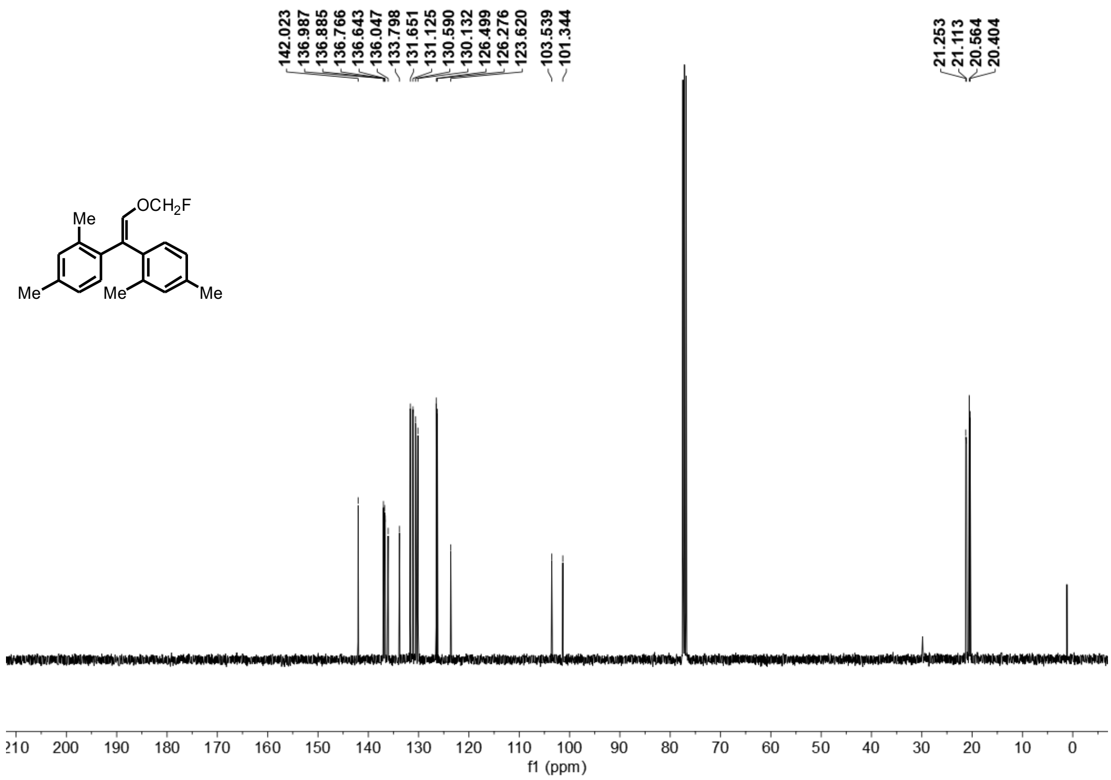
^{19}F NMR Spectrum of Compound **7** (376 MHz, $CDCl_3$)



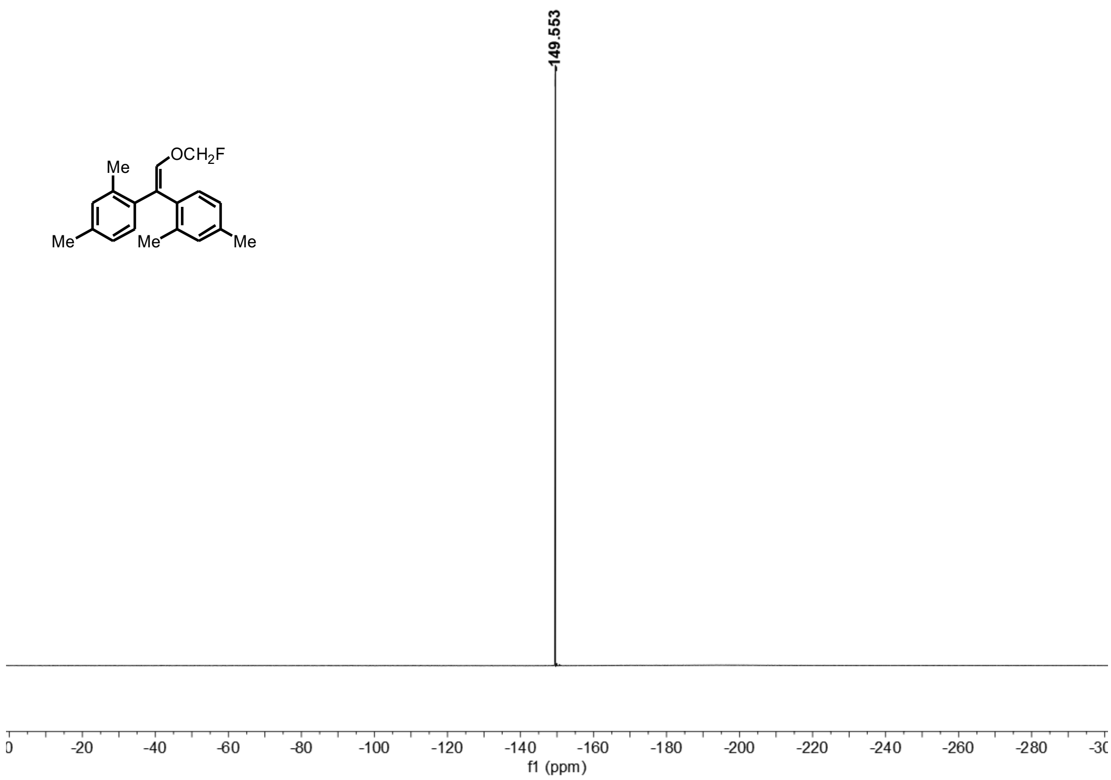
^{1}H NMR Spectrum of Compound **8** (400 MHz, $CDCl_3$)



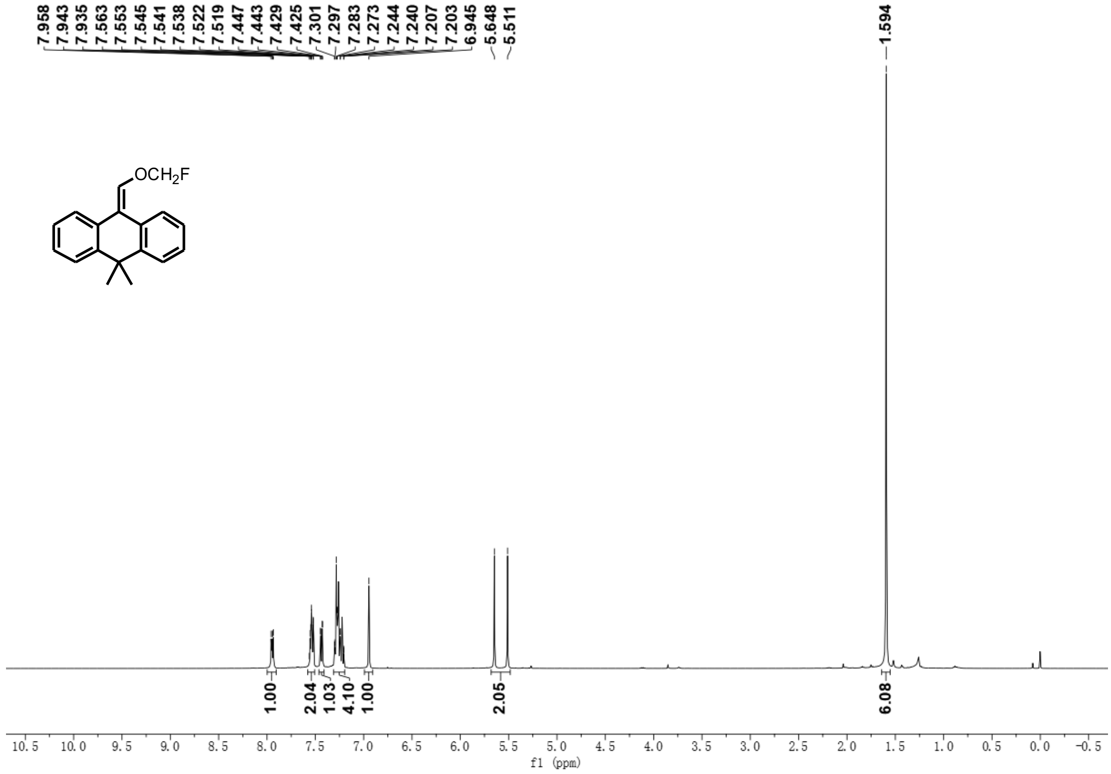
^{13}C NMR Spectrum of Compound **8** (101 MHz, $CDCl_3$)



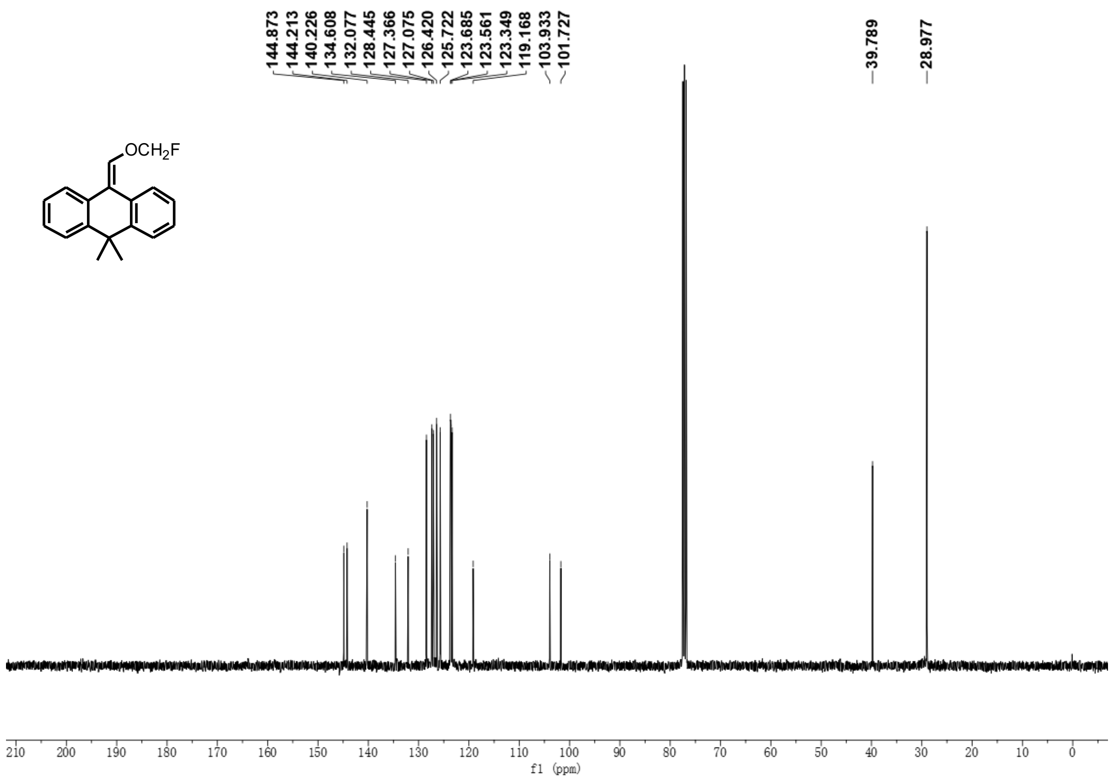
^{19}F NMR Spectrum of Compound **8** (376 MHz, $CDCl_3$)



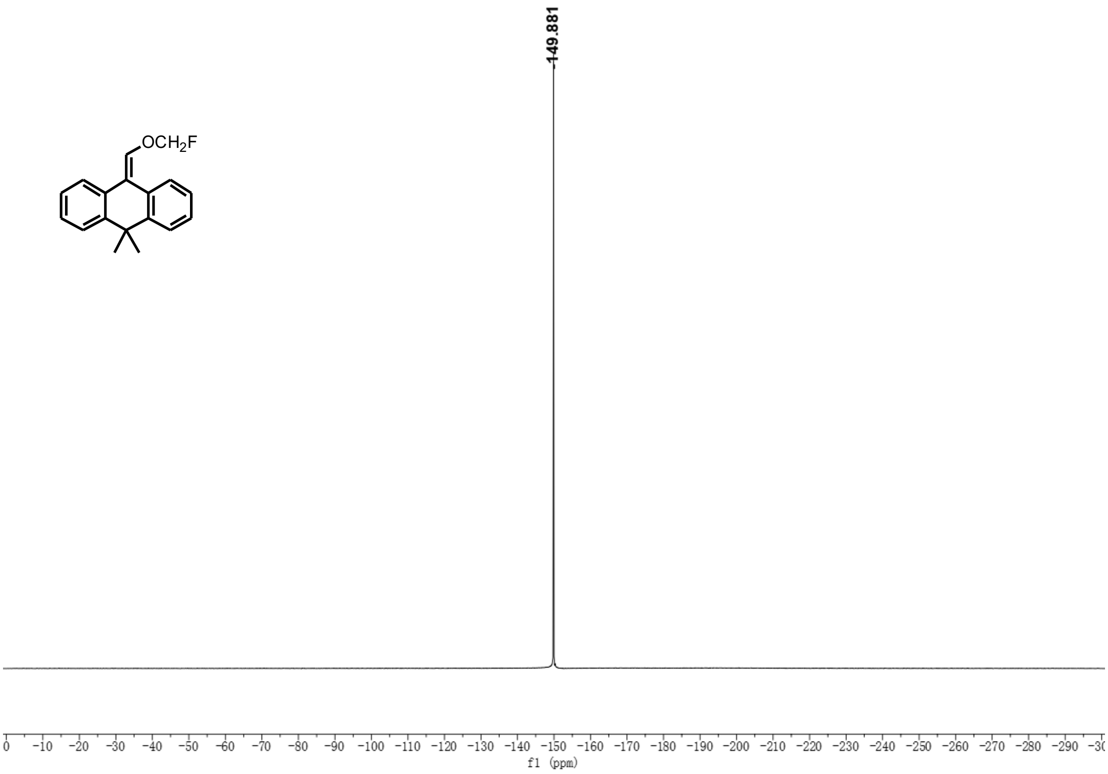
[1]H NMR Spectrum of Compound **9** (400 MHz, $CDCl_3$)



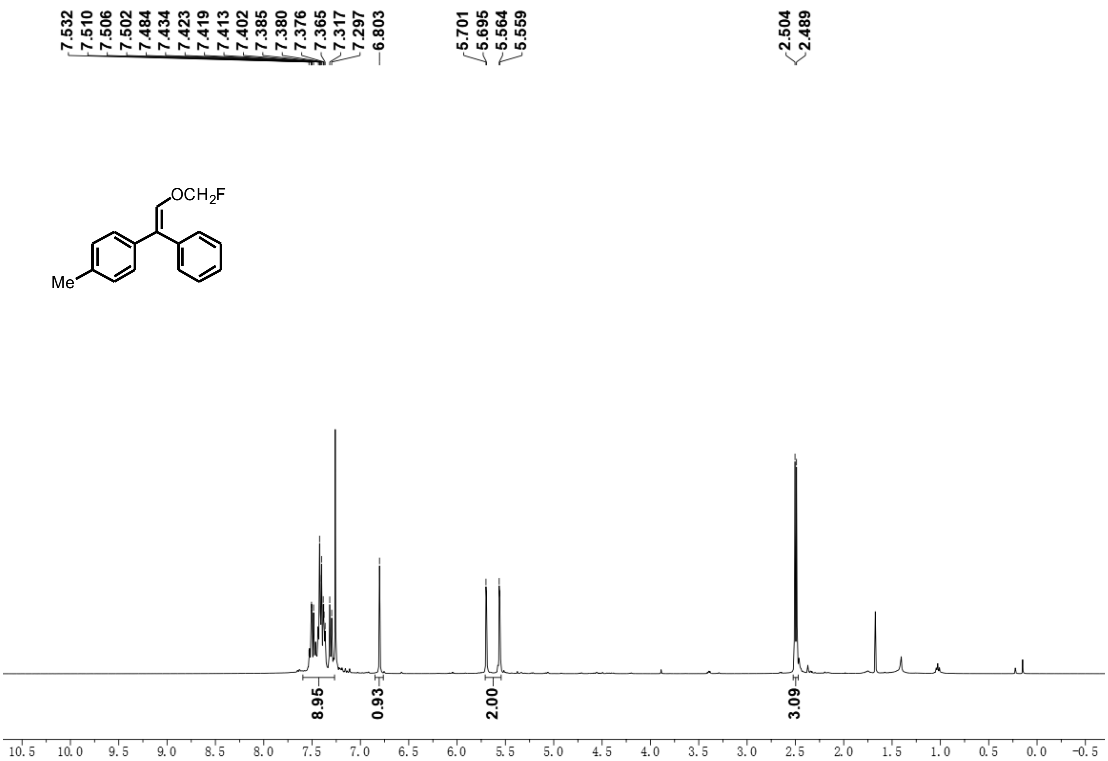
[13]C NMR Spectrum of Compound **9** (101 MHz, $CDCl_3$)



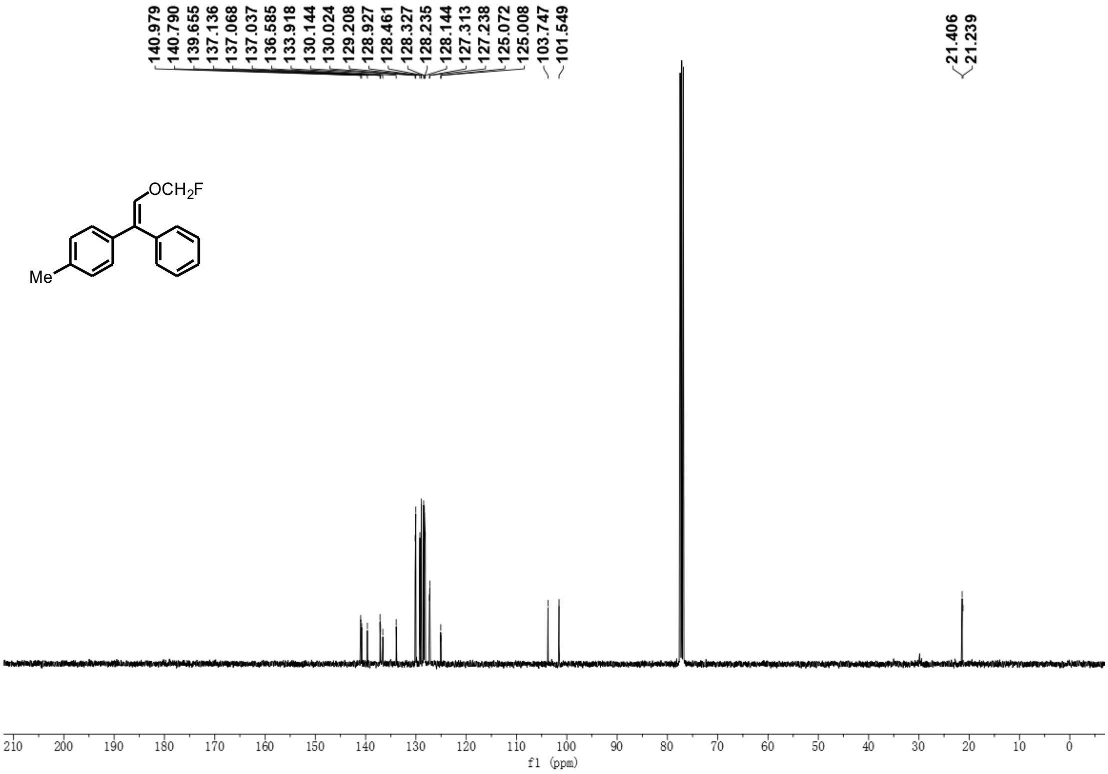
^{19}F NMR Spectrum of Compound **9** (376 MHz, $CDCl_3$)



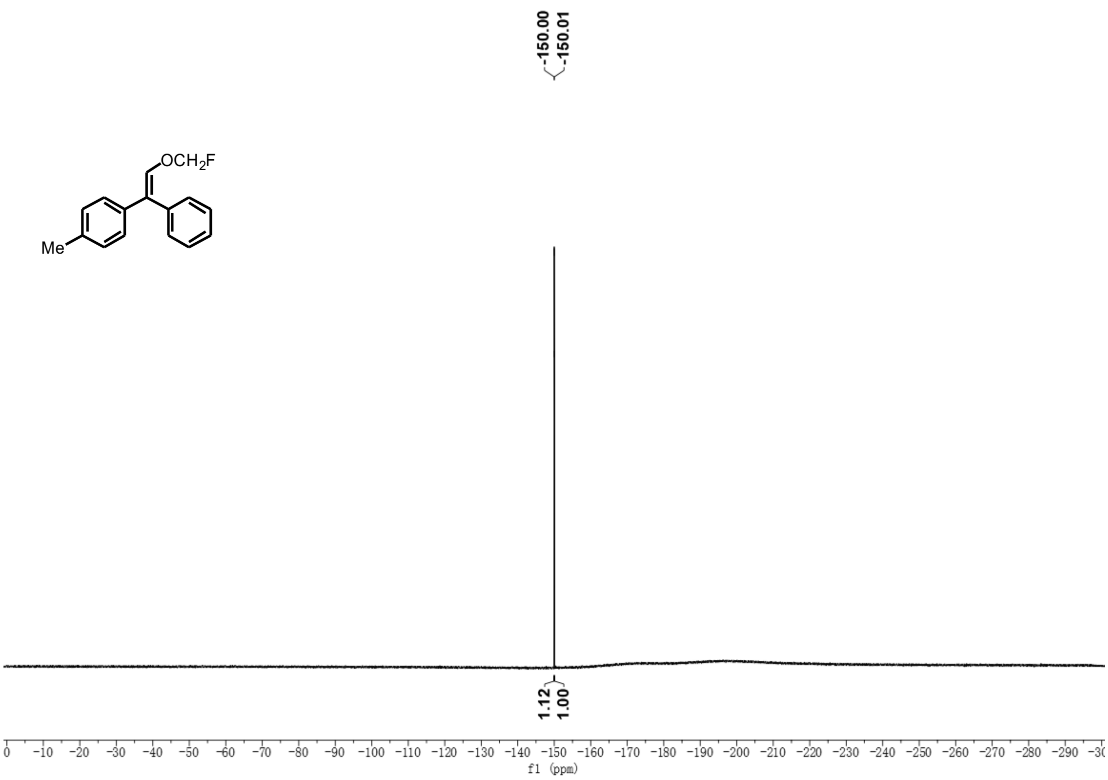
^{1}H NMR Spectrum of Compound **10** (400 MHz, $CDCl_3$)



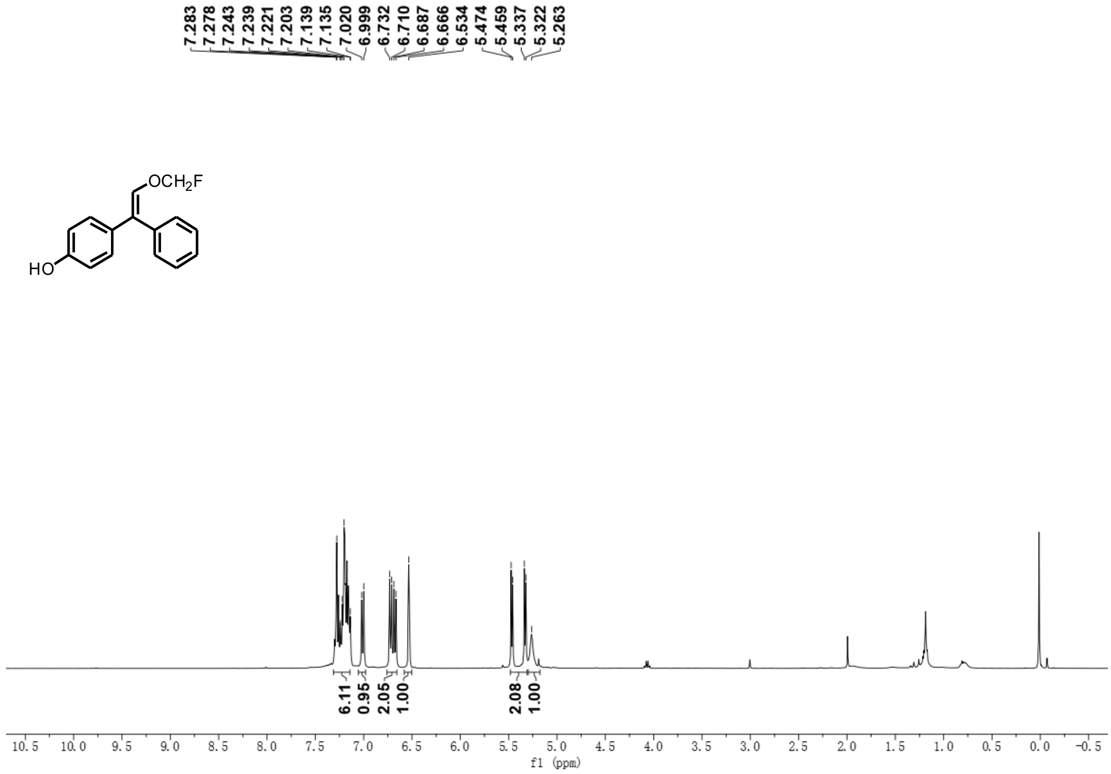
^{13}C NMR Spectrum of Compound **10** (101 MHz, $CDCl_3$)



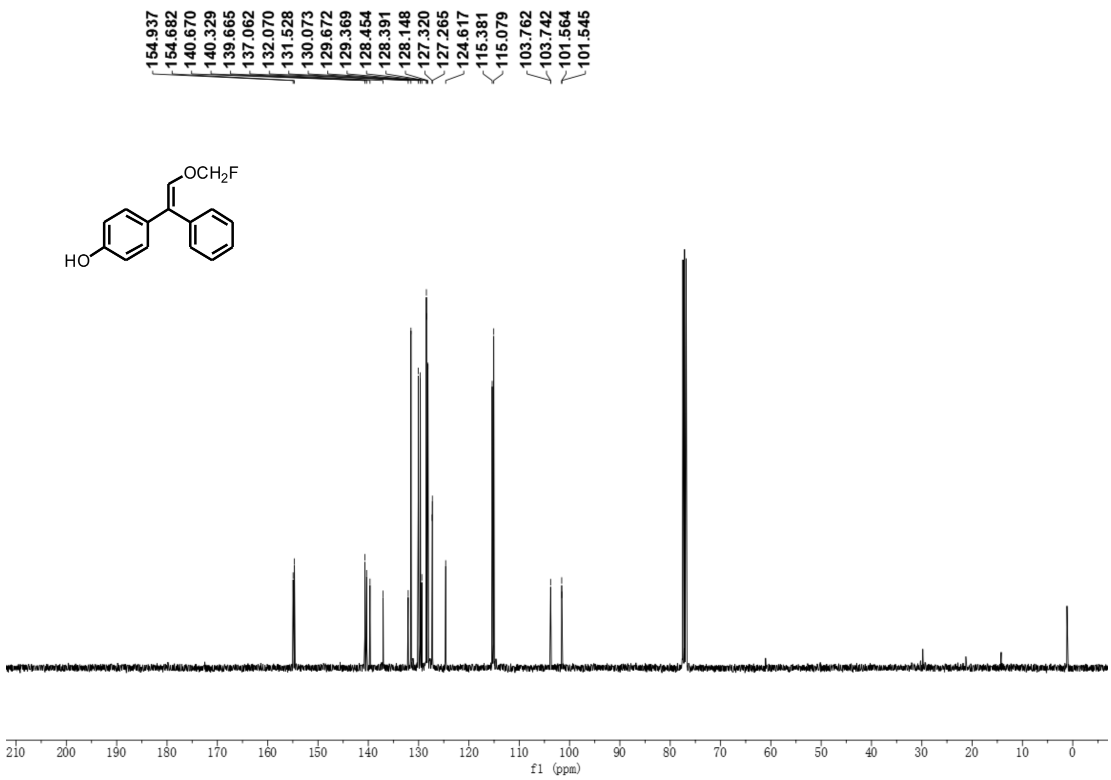
^{19}F NMR Spectrum of Compound **10** (376 MHz, $CDCl_3$)



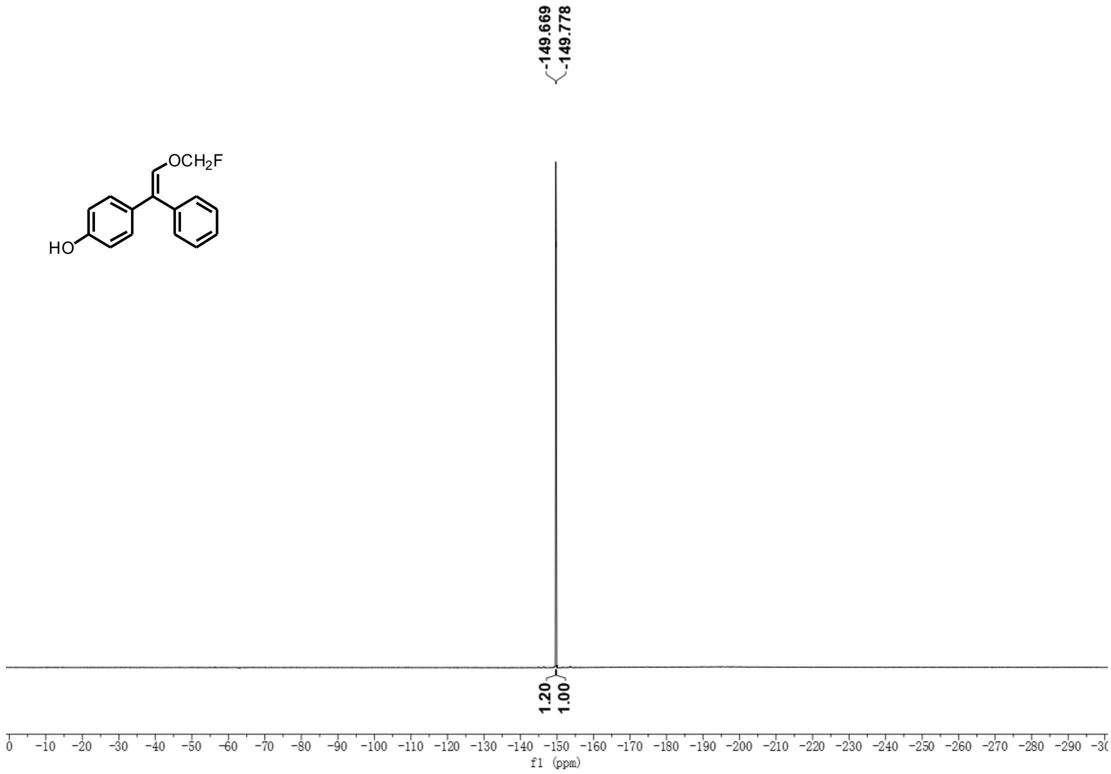
[1]H NMR Spectrum of Compound **11** (400 MHz, $CDCl_3$)



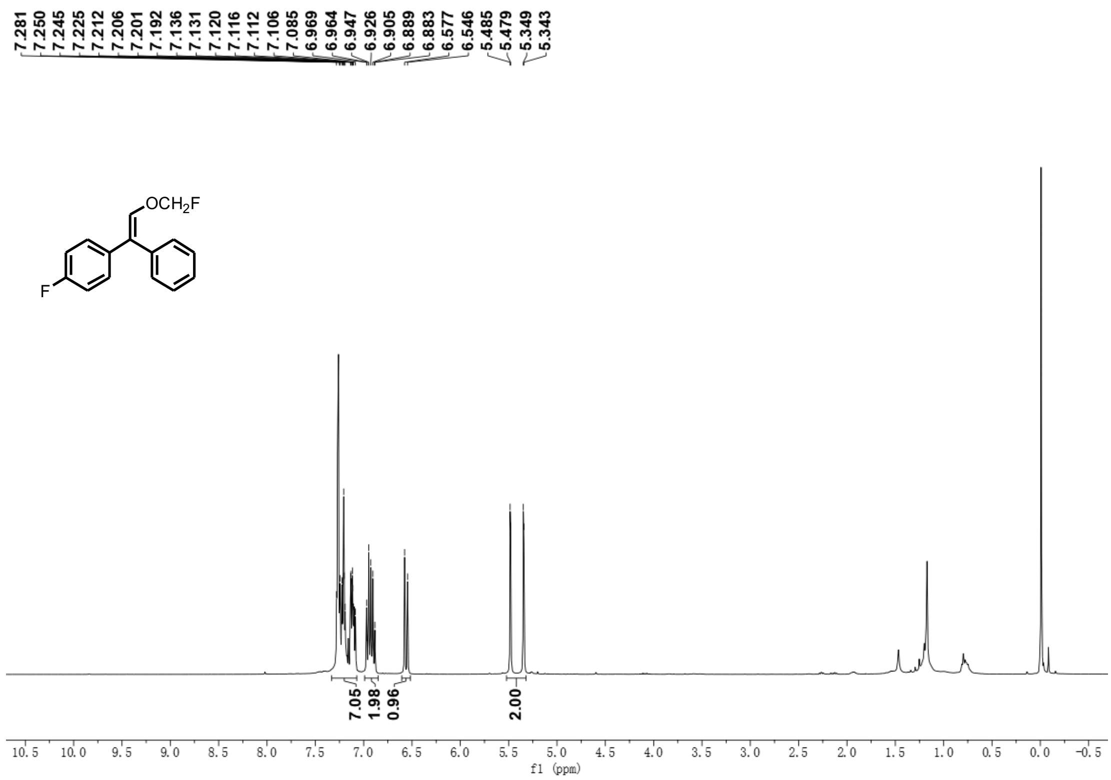
[13]C NMR Spectrum of Compound **11** (101 MHz, $CDCl_3$)



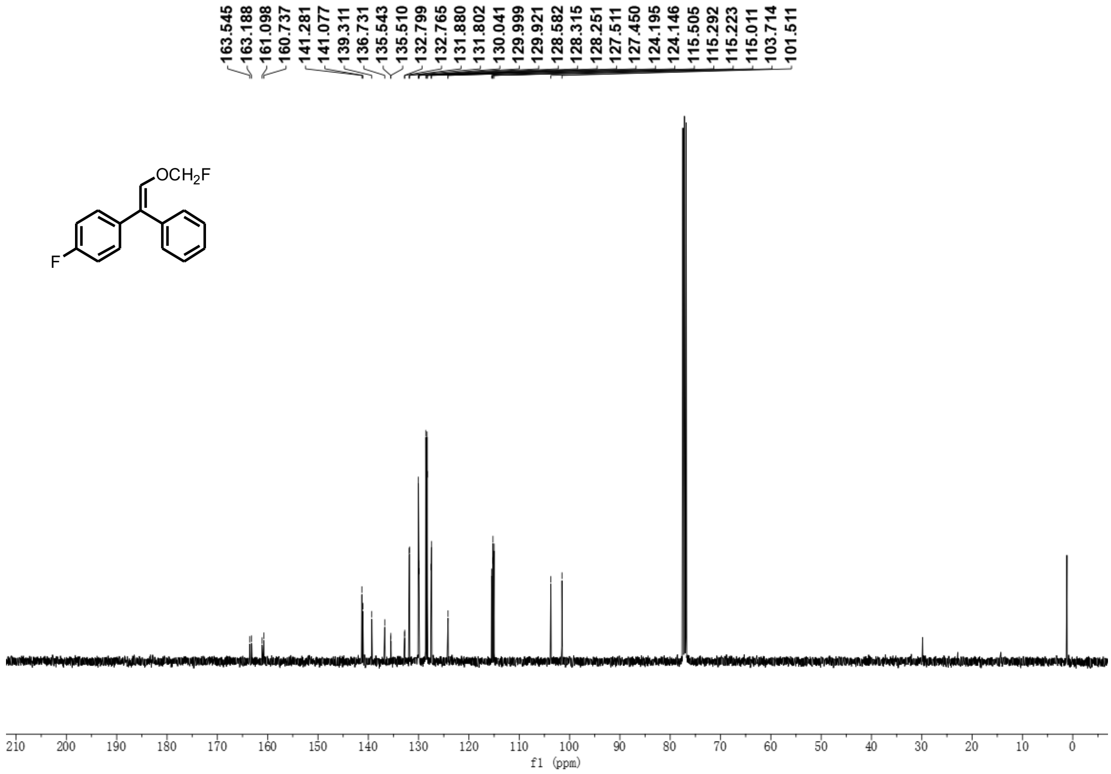
^{19}F NMR Spectrum of Compound **11** (376 MHz, $CDCl_3$)



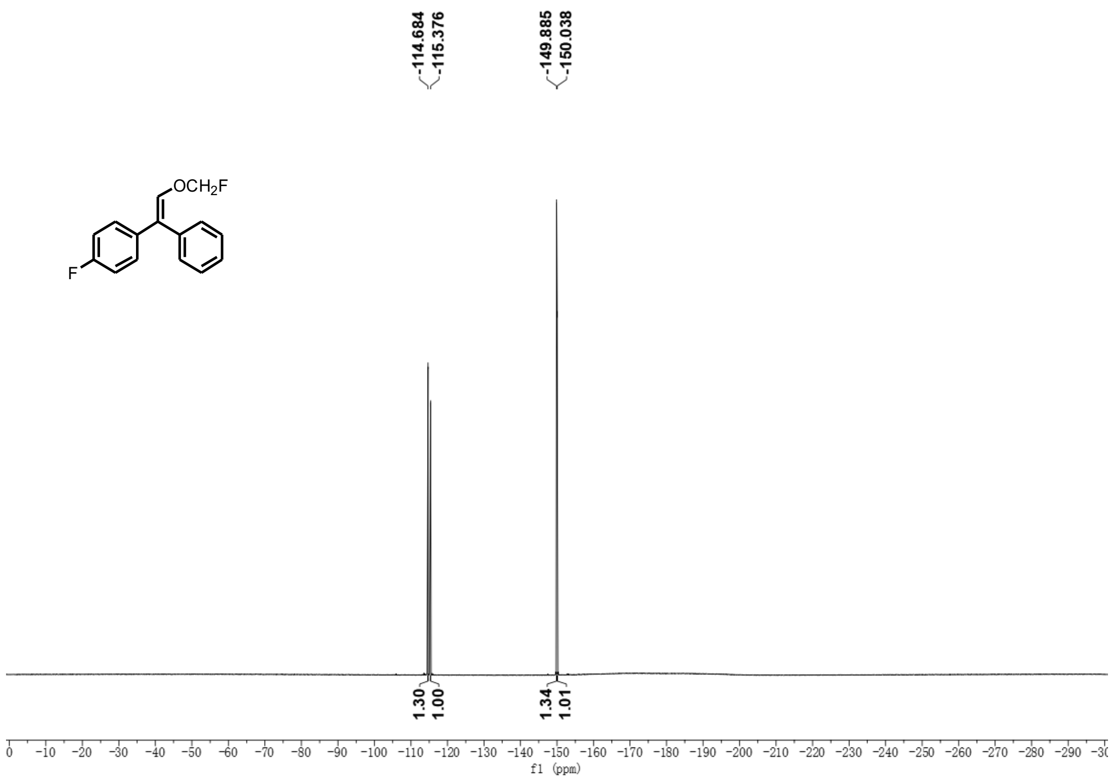
^{1}H NMR Spectrum of Compound **12** (400 MHz, $CDCl_3$)



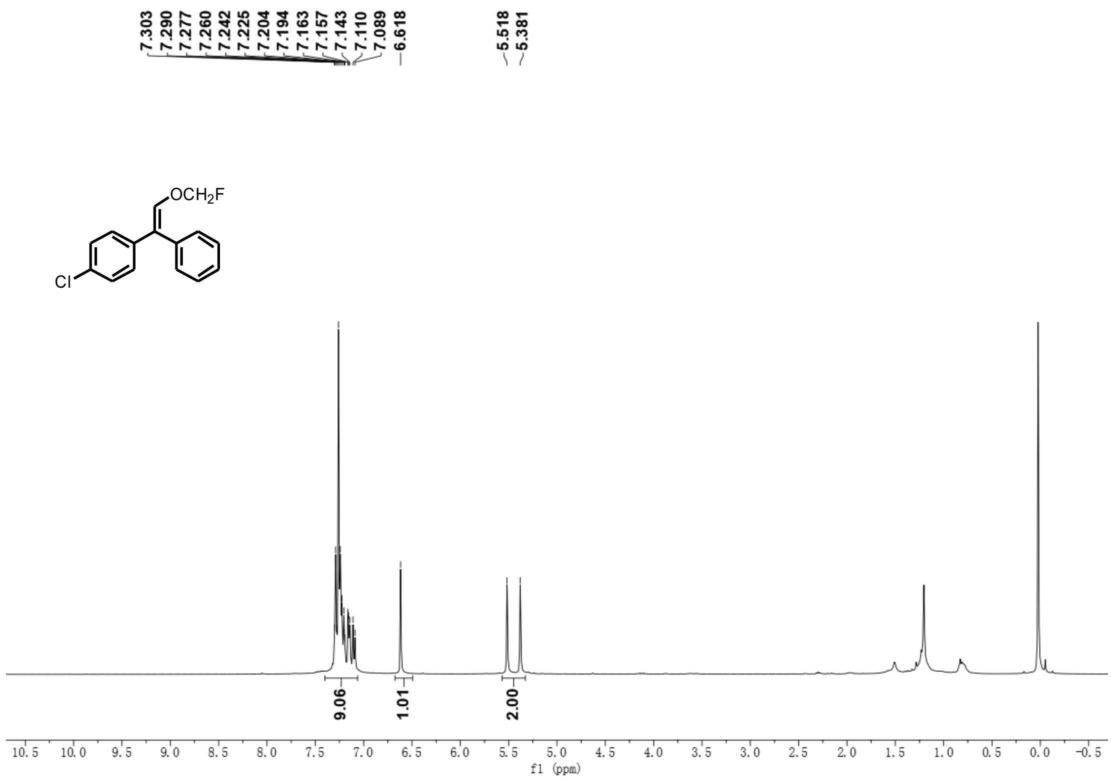
^{13}C NMR Spectrum of Compound **12** (101 MHz, $CDCl_3$)



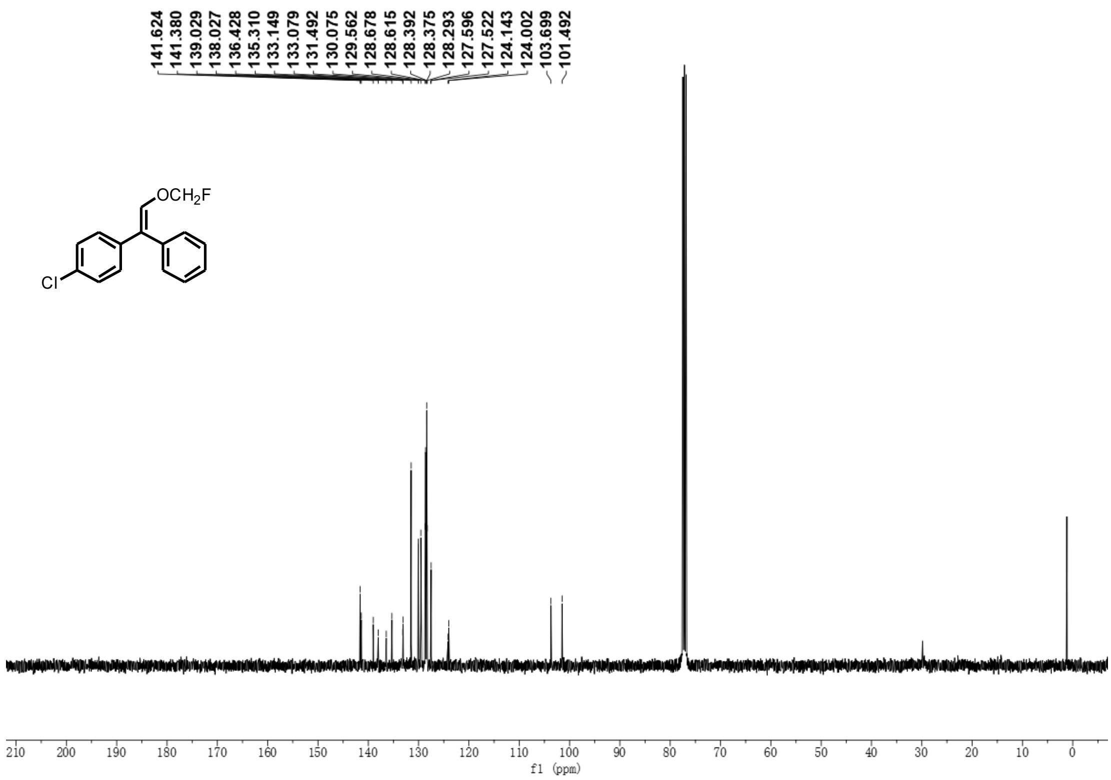
^{19}F NMR Spectrum of Compound **12** (376 MHz, $CDCl_3$)



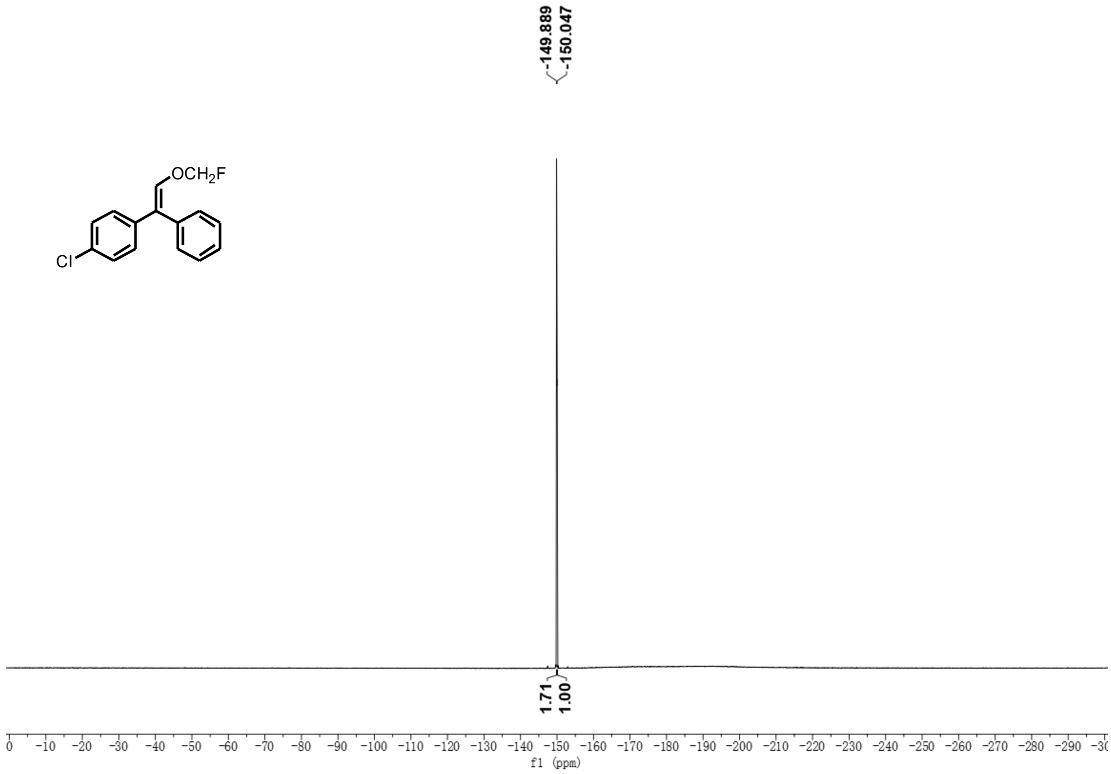
^{1}H NMR Spectrum of Compound **13** (400 MHz, $CDCl_3$)



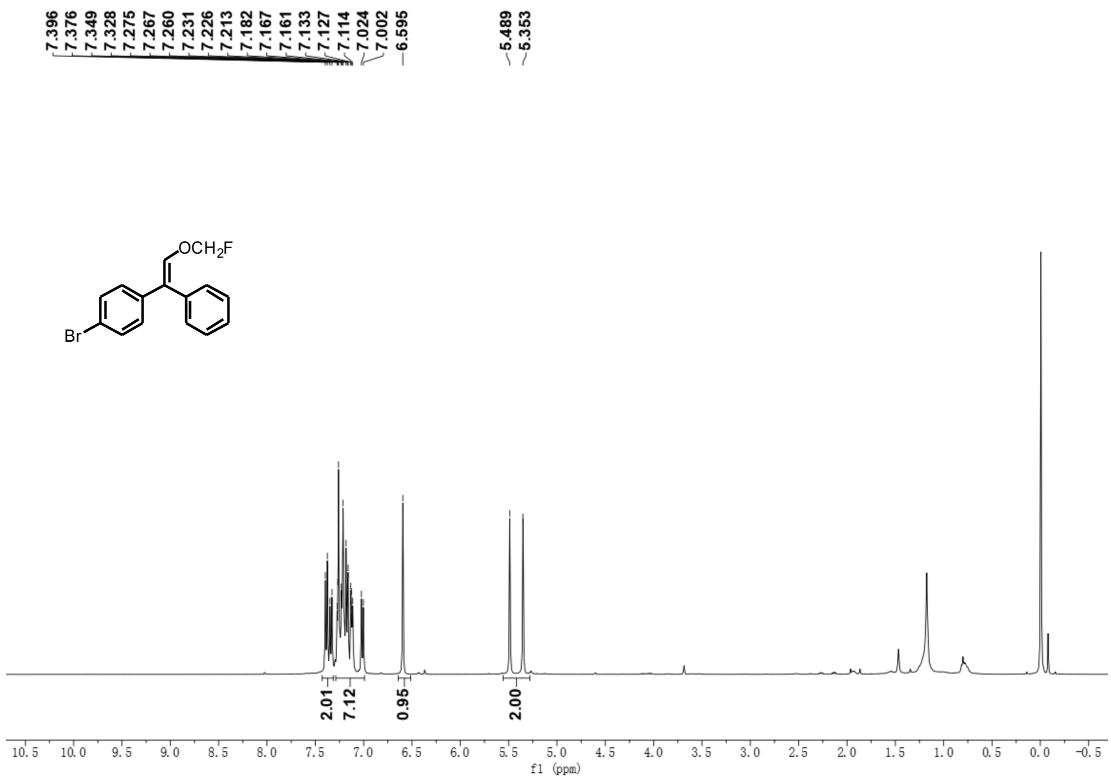
^{13}C NMR Spectrum of Compound **13** (101 MHz, $CDCl_3$)



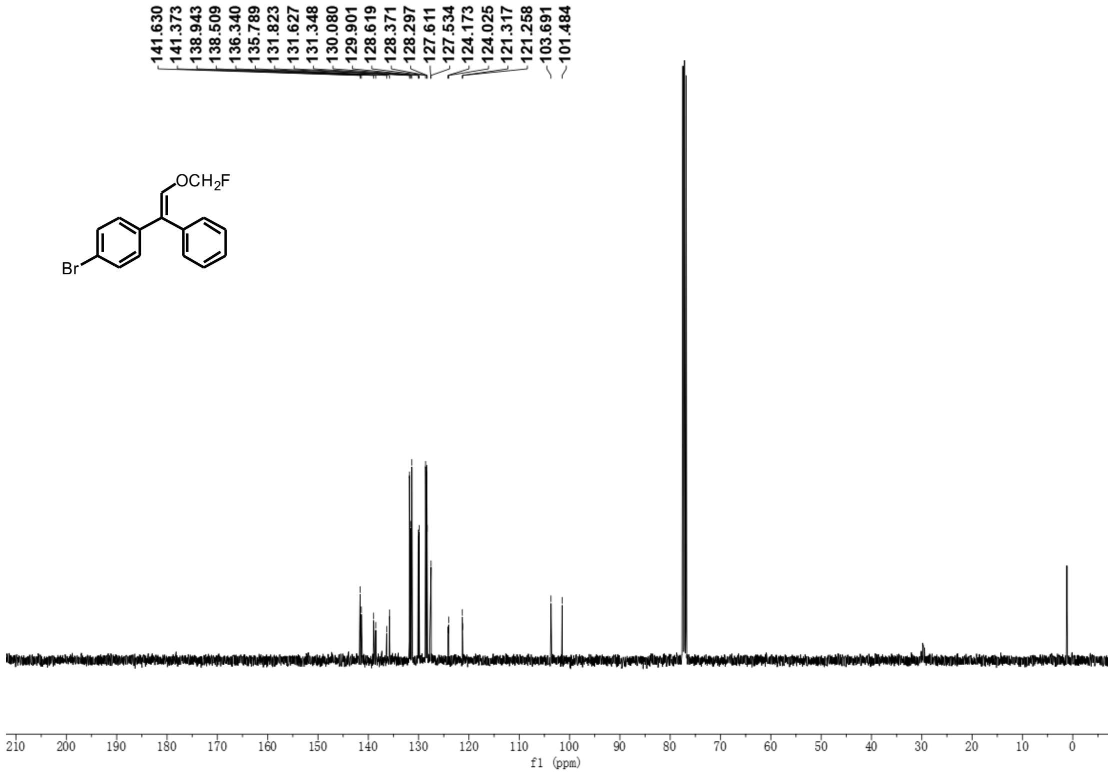
^{19}F NMR Spectrum of Compound **13** (376 MHz, $CDCl_3$)



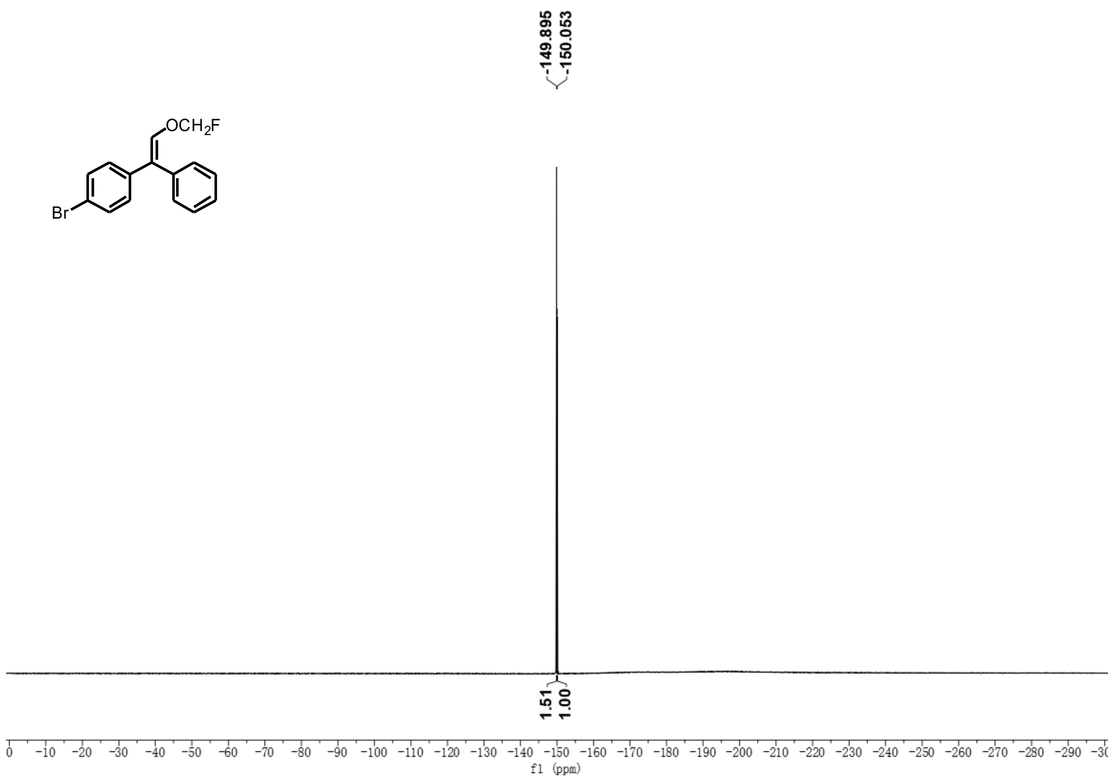
^{1}H NMR Spectrum of Compound **14** (400 MHz, $CDCl_3$)



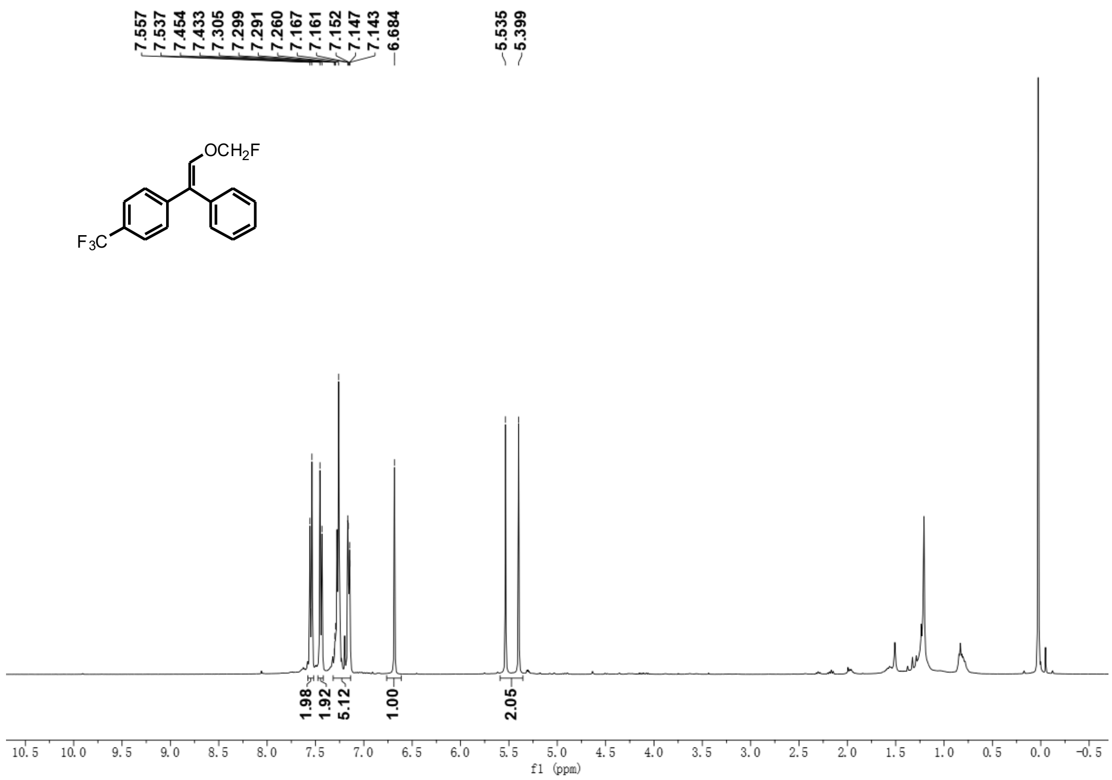
^{13}C NMR Spectrum of Compound **14** (101 MHz, $CDCl_3$)



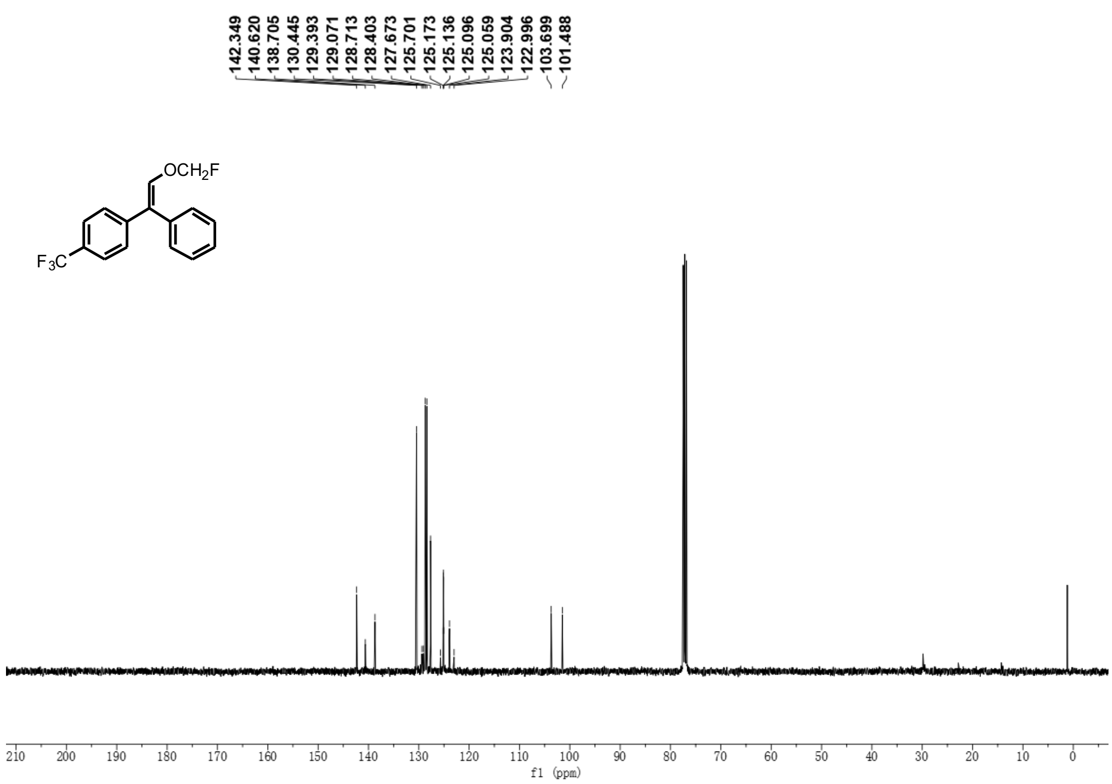
^{19}F NMR Spectrum of Compound **14** (376 MHz, $CDCl_3$)



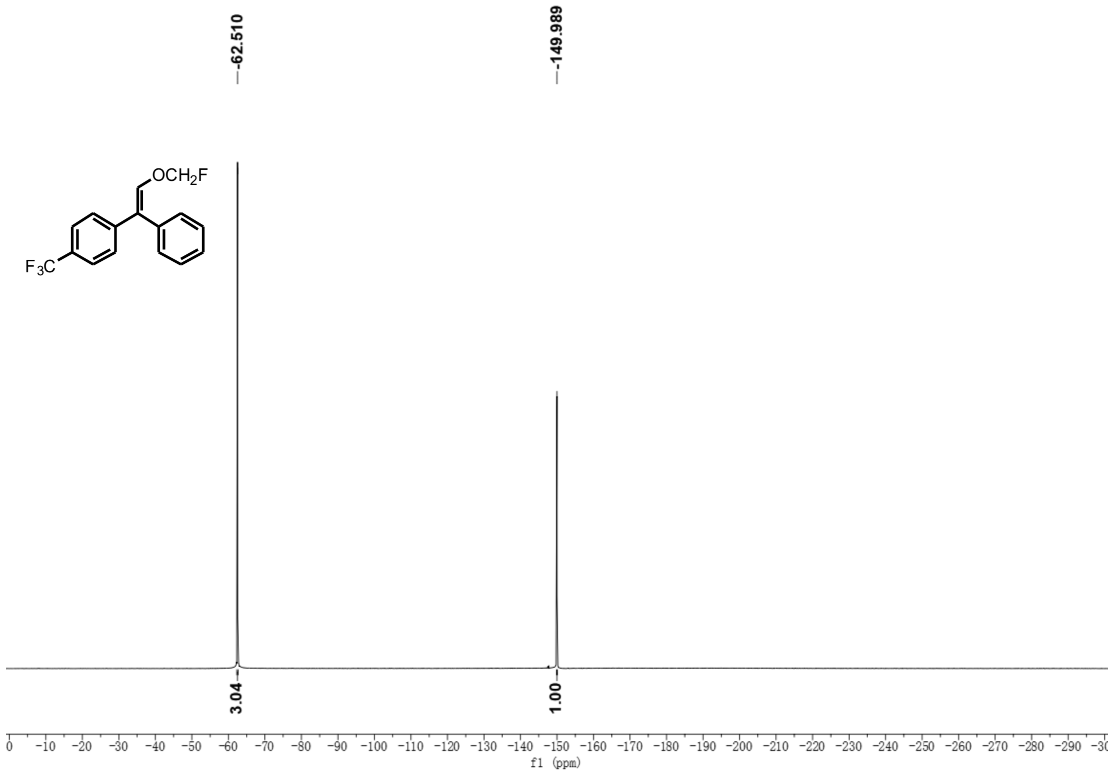
^{1}H NMR Spectrum of Compound **15** (400 MHz, $CDCl_3$)



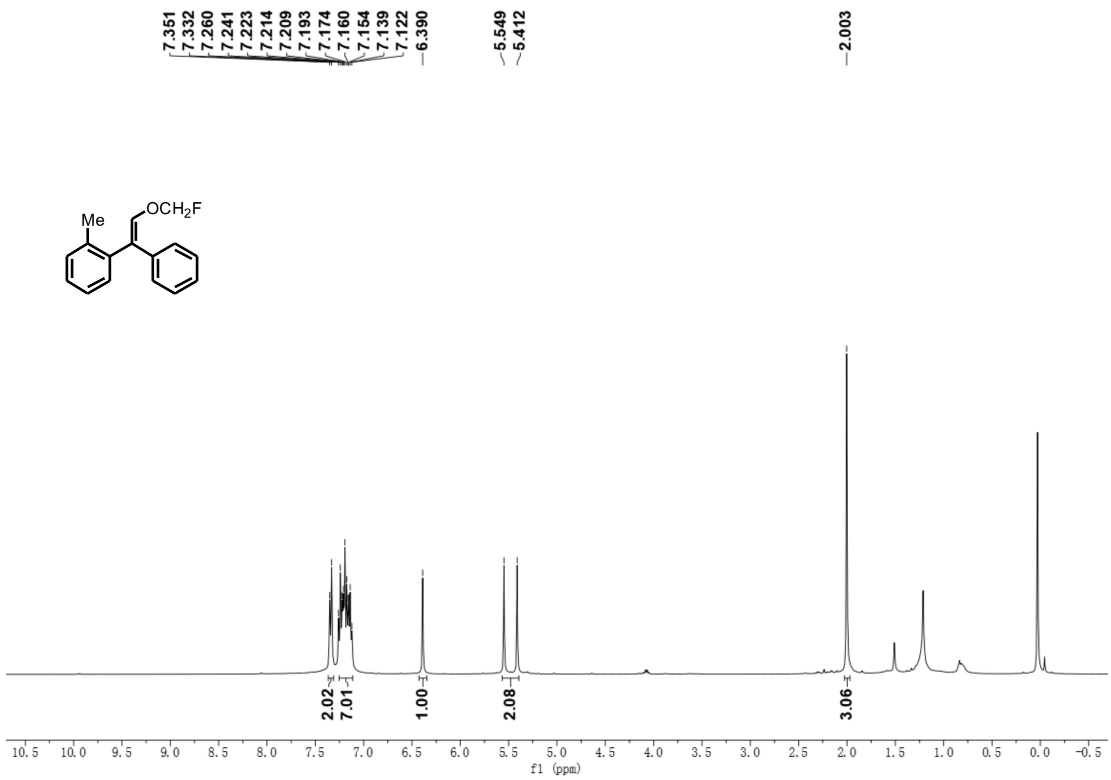
^{13}C NMR Spectrum of Compound **15** (101 MHz, $CDCl_3$)



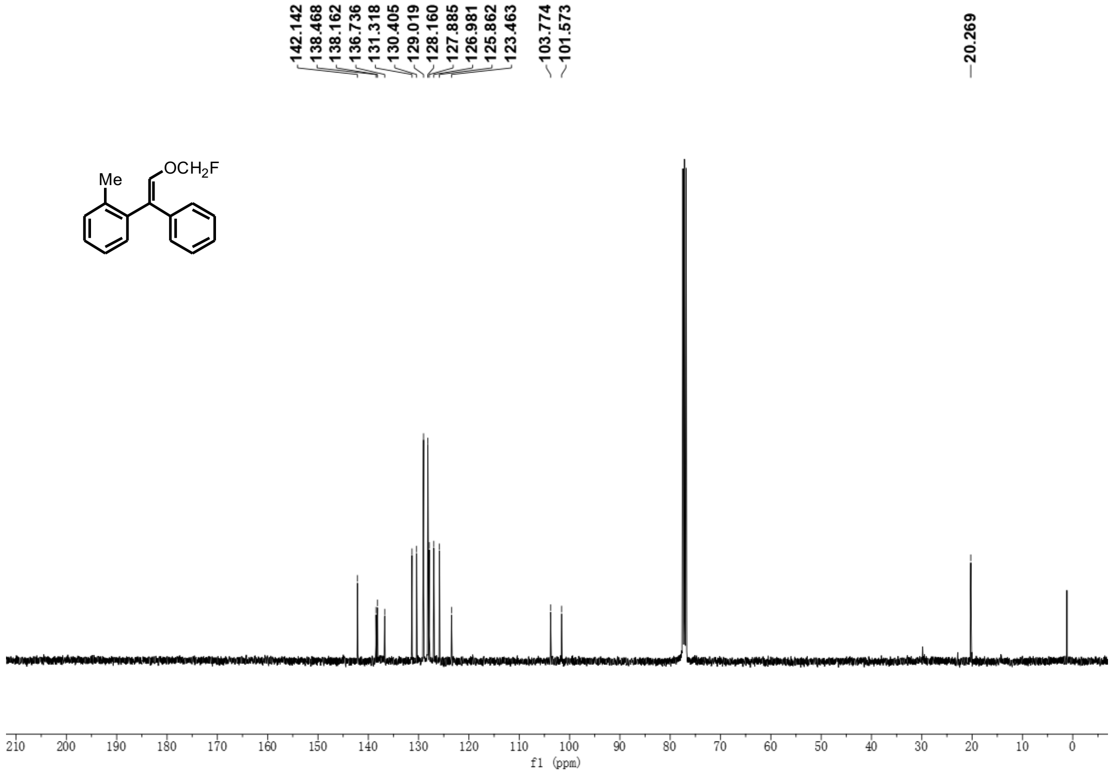
^{19}F NMR Spectrum of Compound **15** (376 MHz, $CDCl_3$)



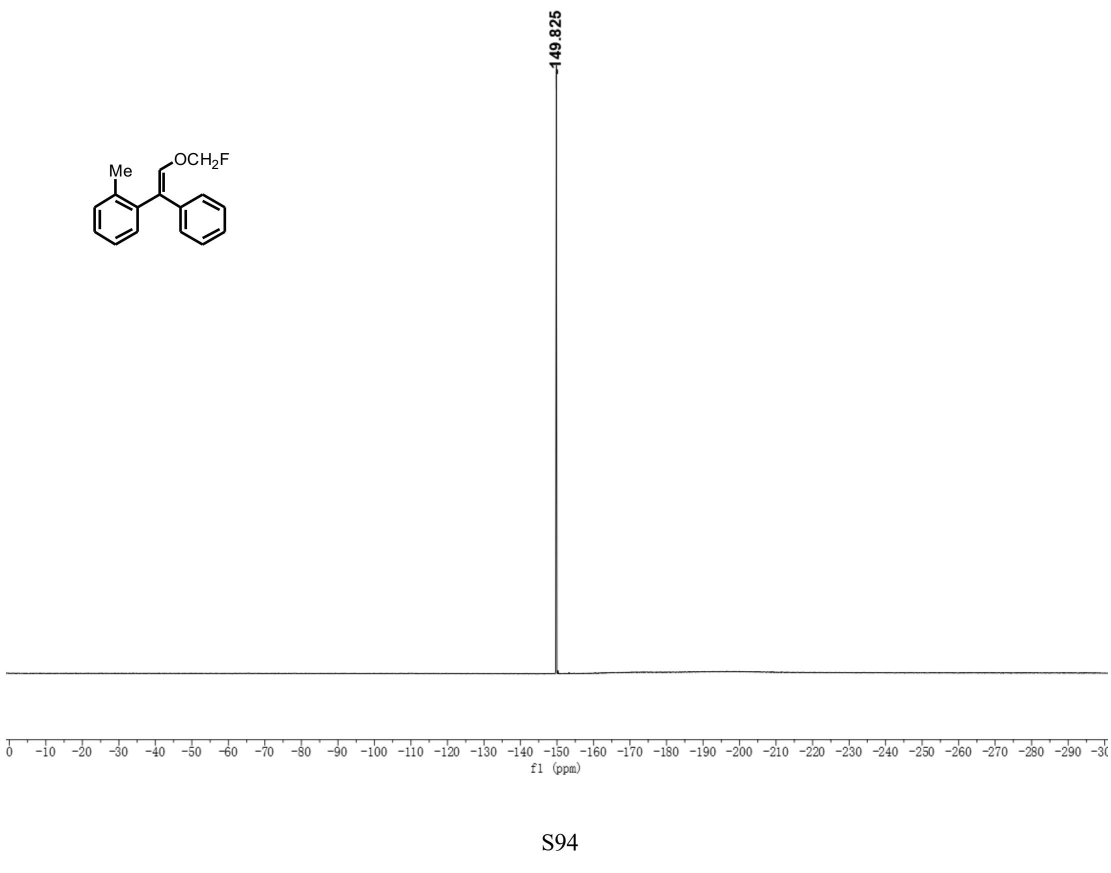
^{1}H NMR Spectrum of Compound **16** (400 MHz, $CDCl_3$)



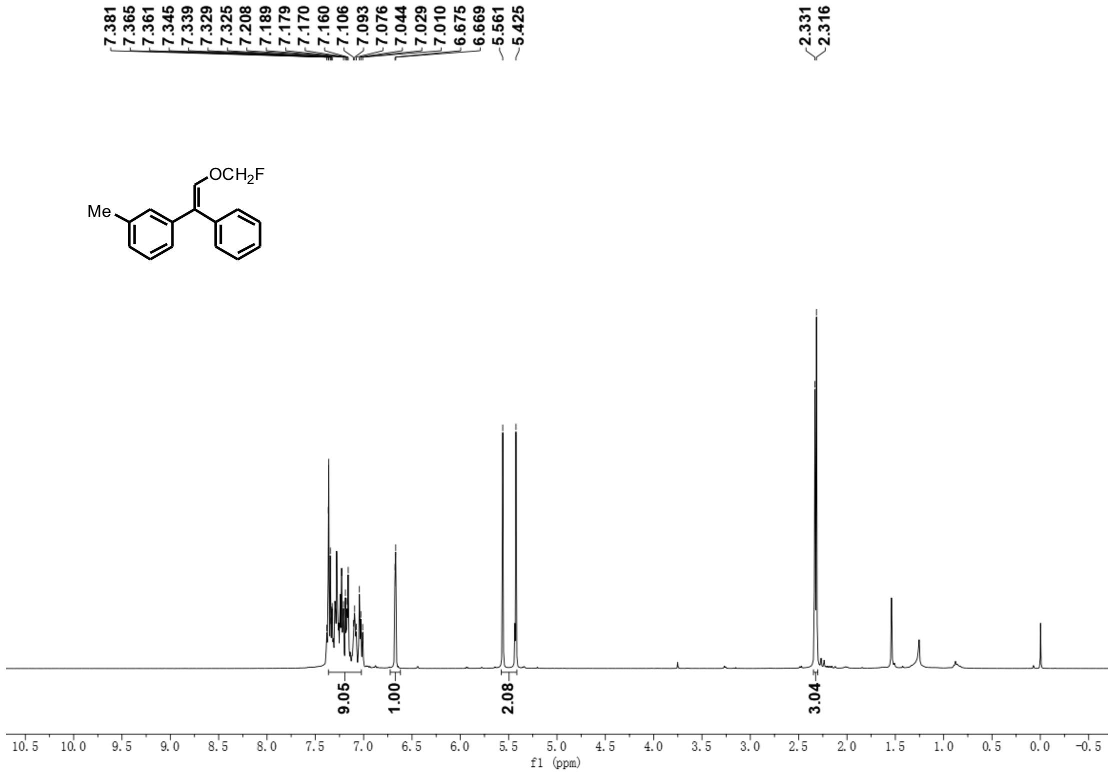
^{13}C NMR Spectrum of Compound **16** (101 MHz, $CDCl_3$)



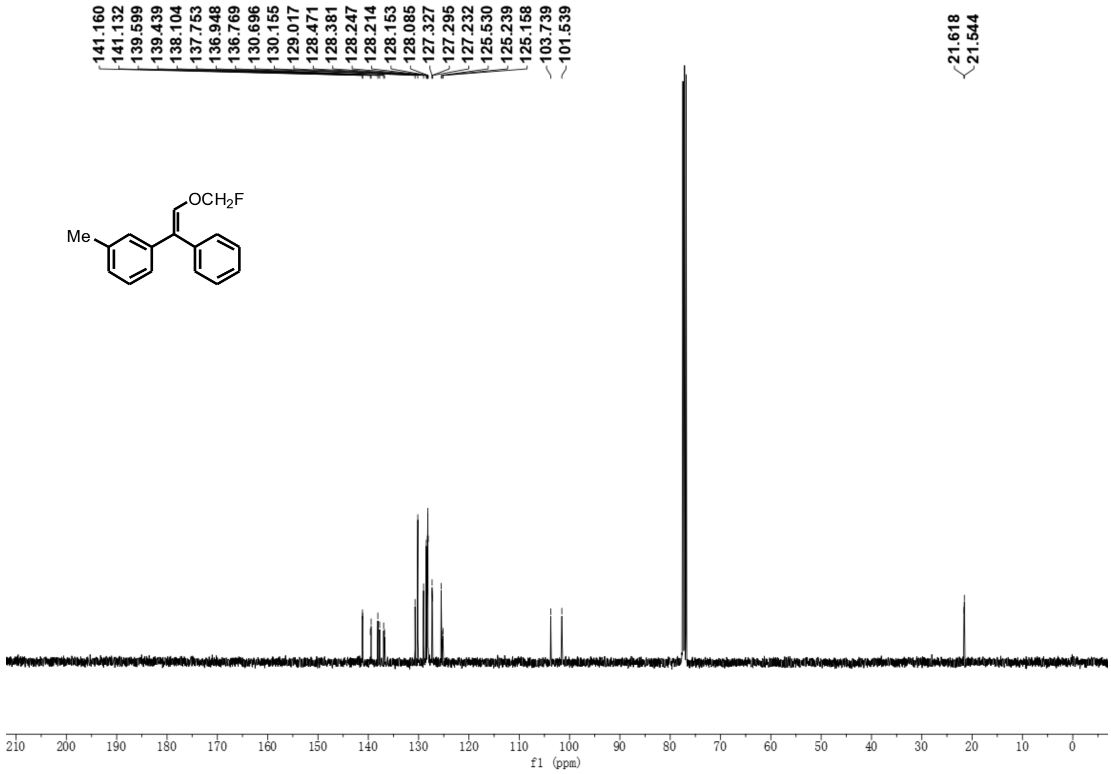
^{19}F NMR Spectrum of Compound **16** (376 MHz, $CDCl_3$)



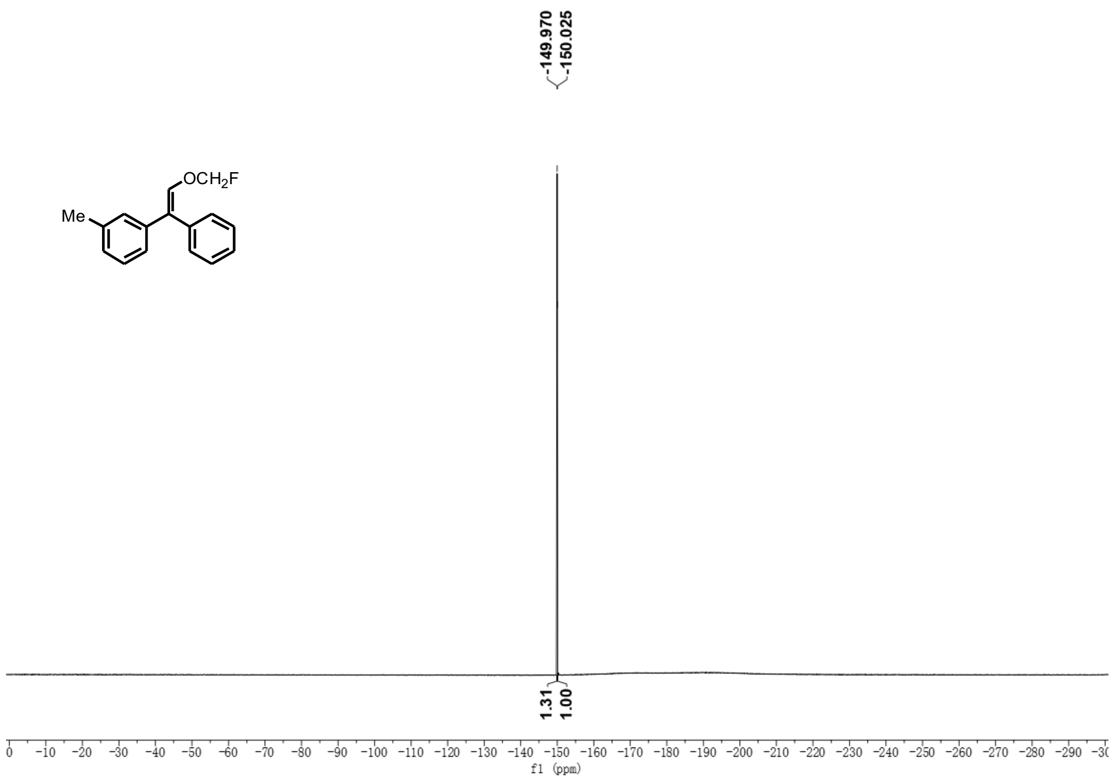
^{1}H NMR Spectrum of Compound **17** (400 MHz, $CDCl_3$)



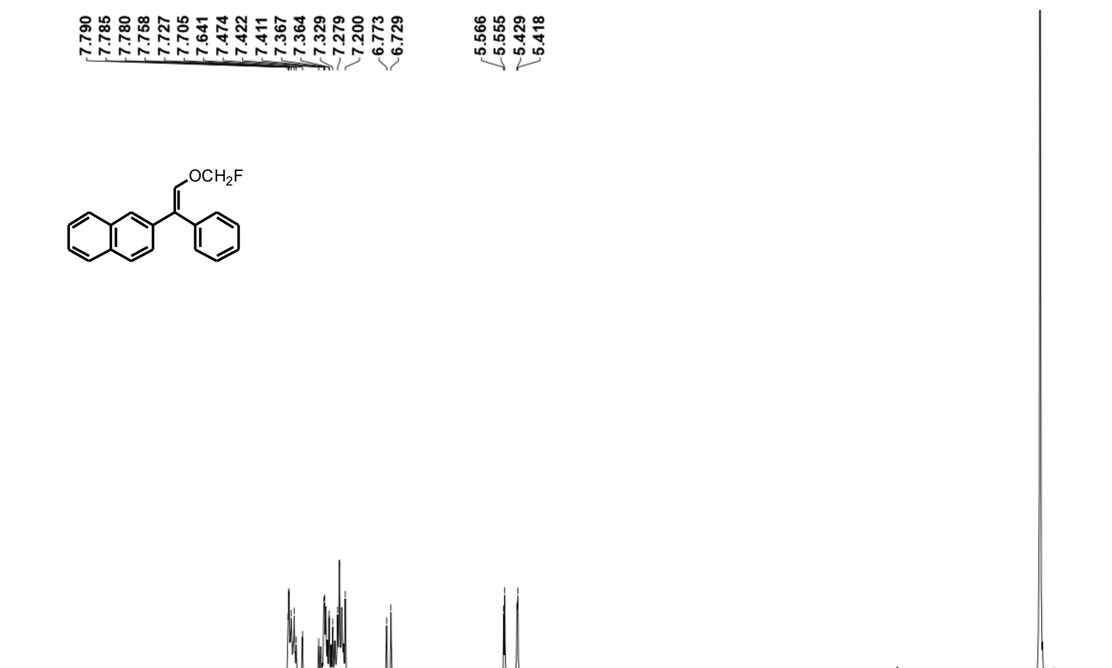
^{13}C NMR Spectrum of Compound **17** (101 MHz, $CDCl_3$)



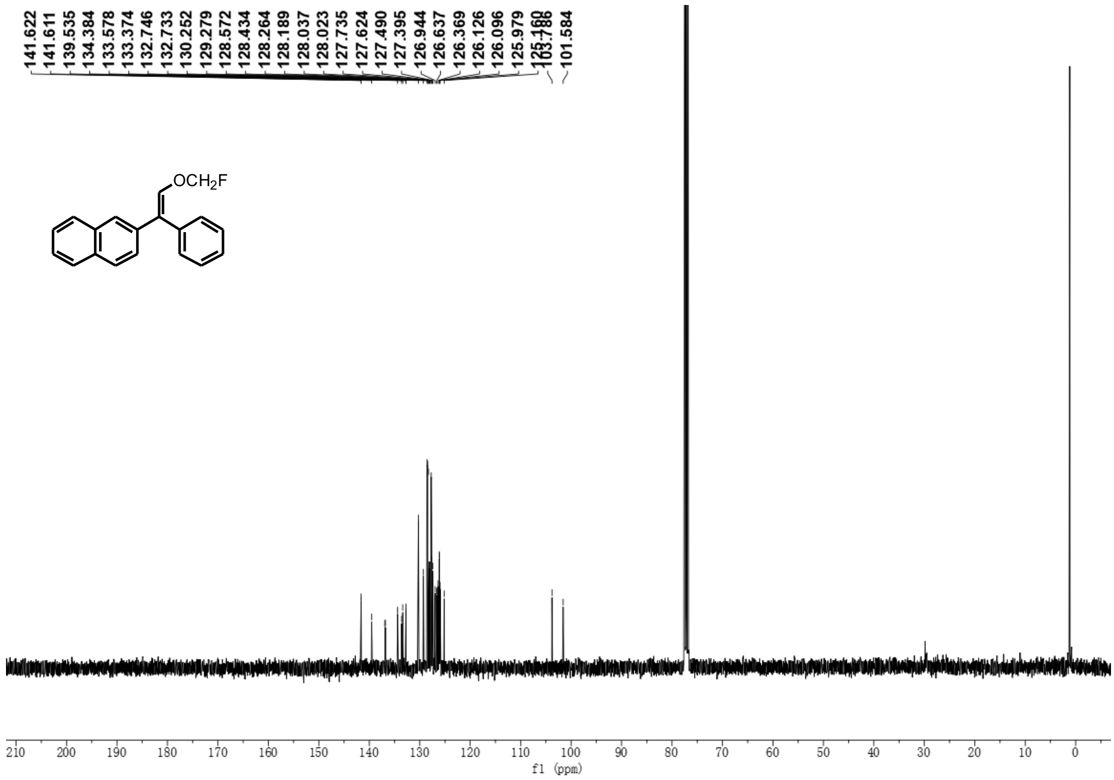
^{19}F NMR Spectrum of Compound **17** (376 MHz, $CDCl_3$)



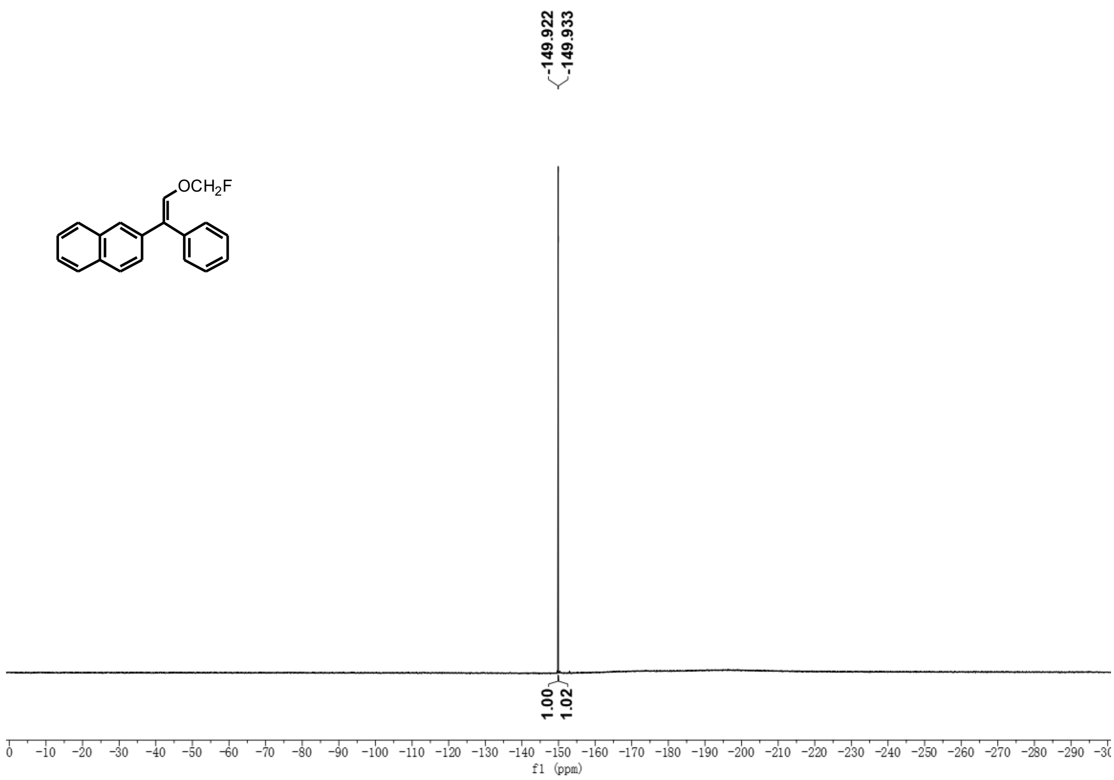
^{1}H NMR Spectrum of Compound **18** (400 MHz, $CDCl_3$)



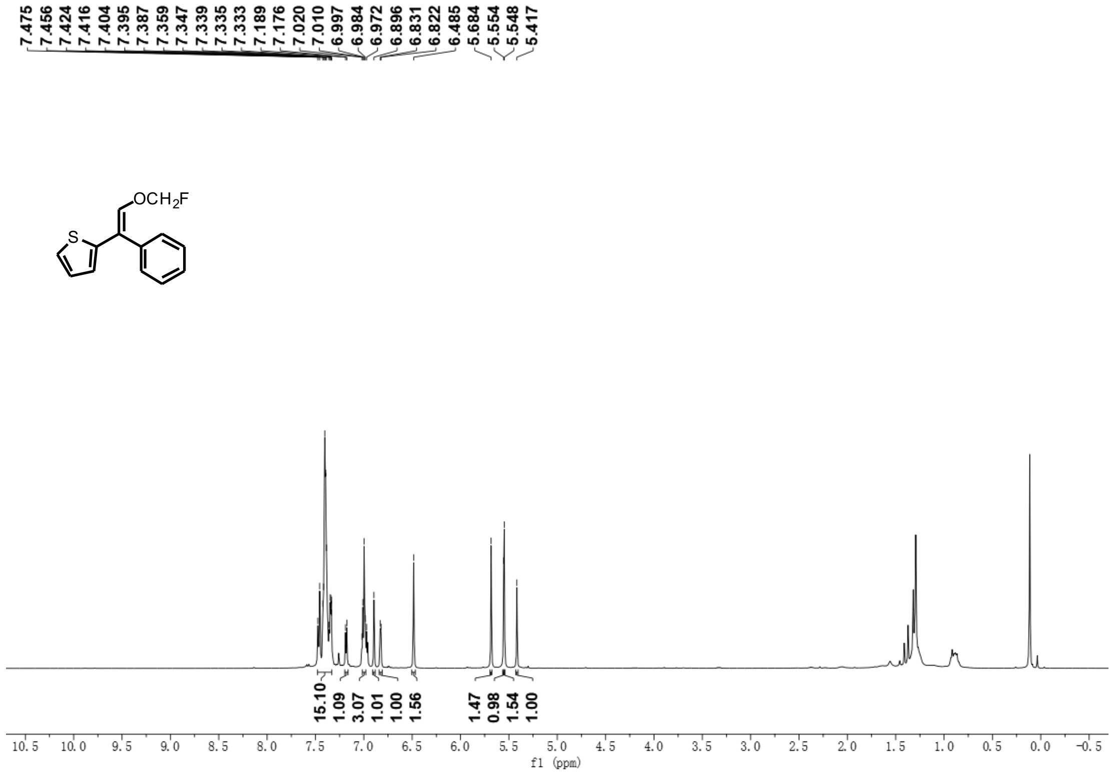
^{13}C NMR Spectrum of Compound **18** (101 MHz, $CDCl_3$)



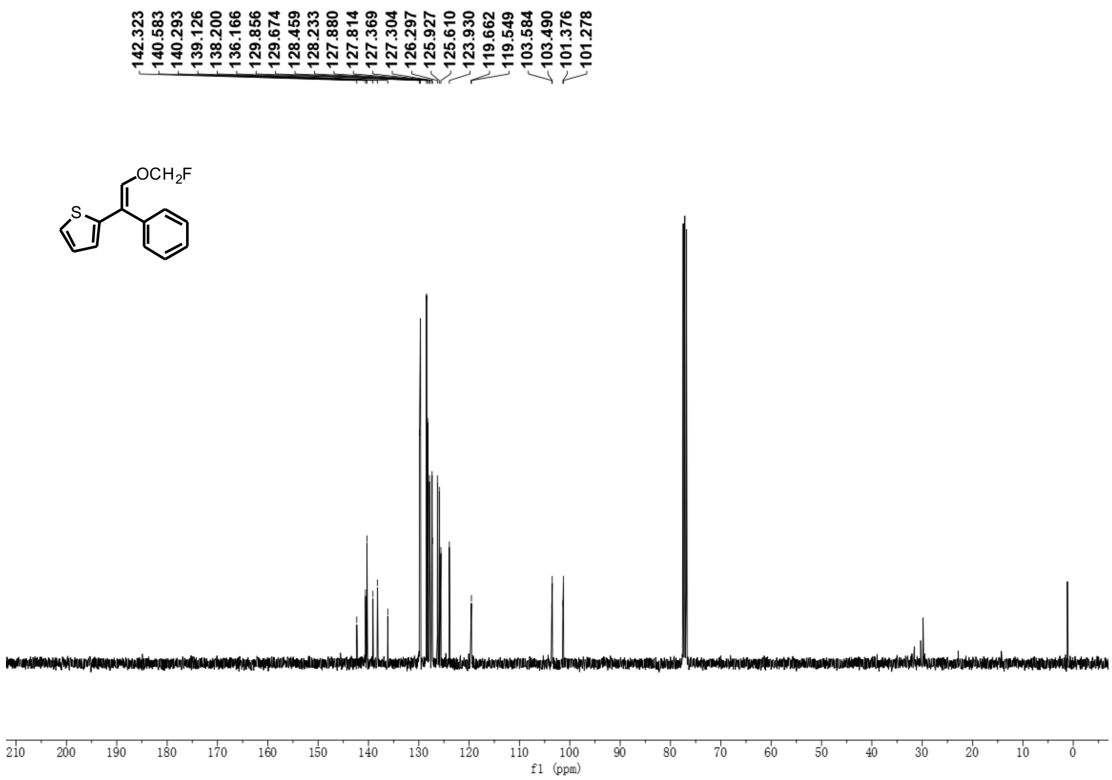
^{19}F NMR Spectrum of Compound **18** (376 MHz, $CDCl_3$)



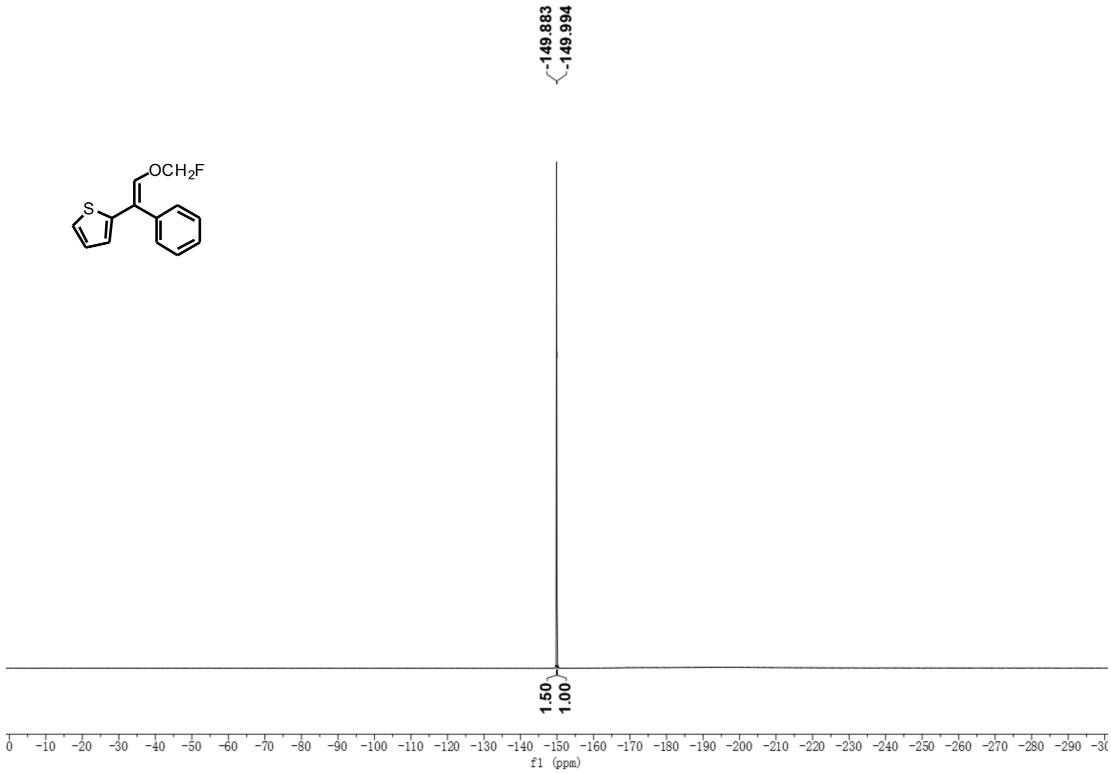
[1]H NMR Spectrum of Compound **19** (400 MHz, $CDCl_3$)



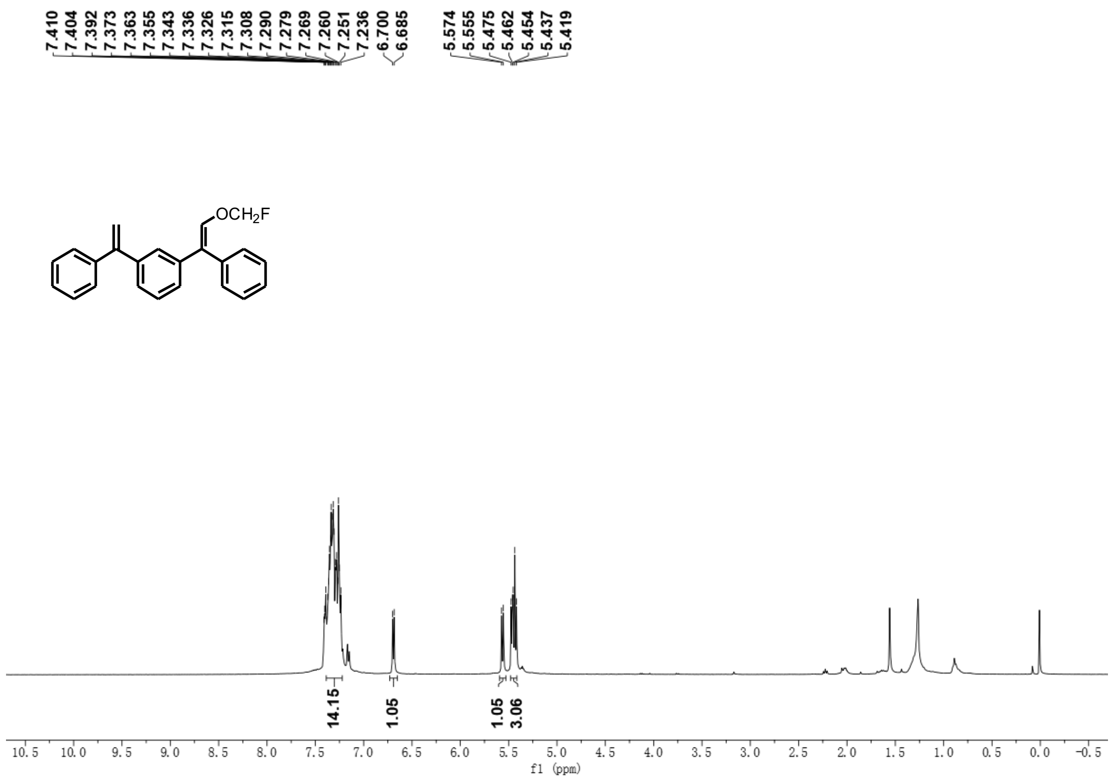
[13]C NMR Spectrum of Compound **19** (101 MHz, $CDCl_3$)



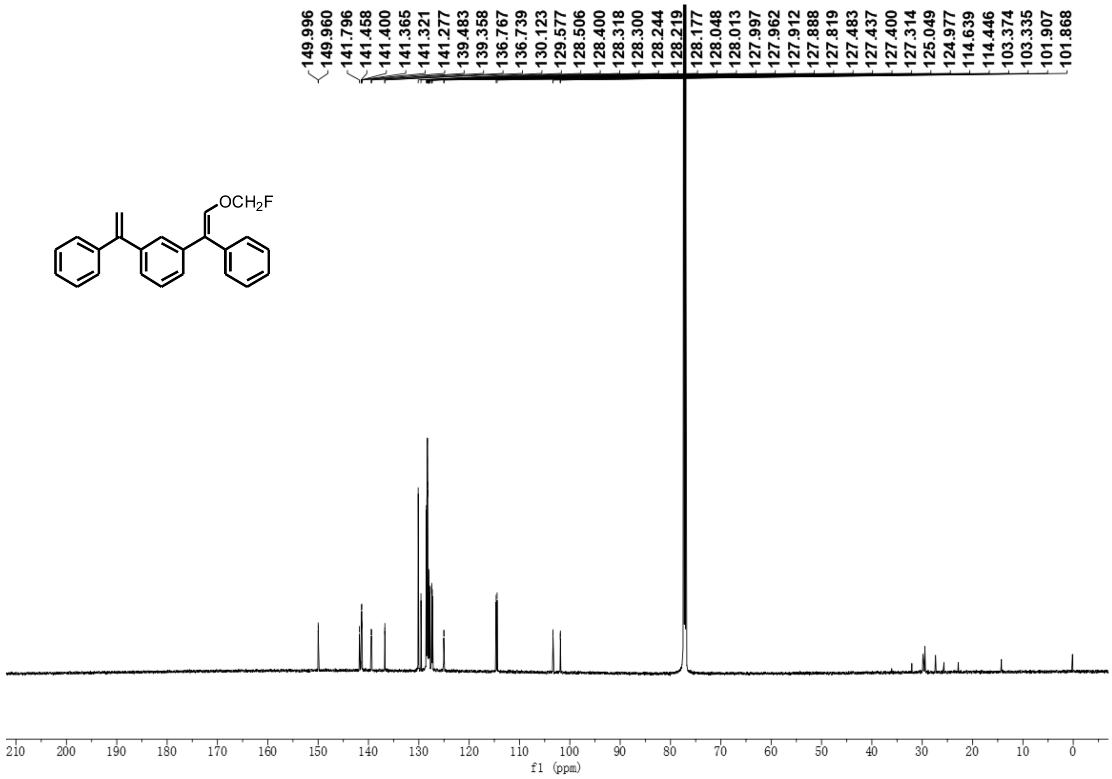
^{19}F NMR Spectrum of Compound **19** (376 MHz, $CDCl_3$)



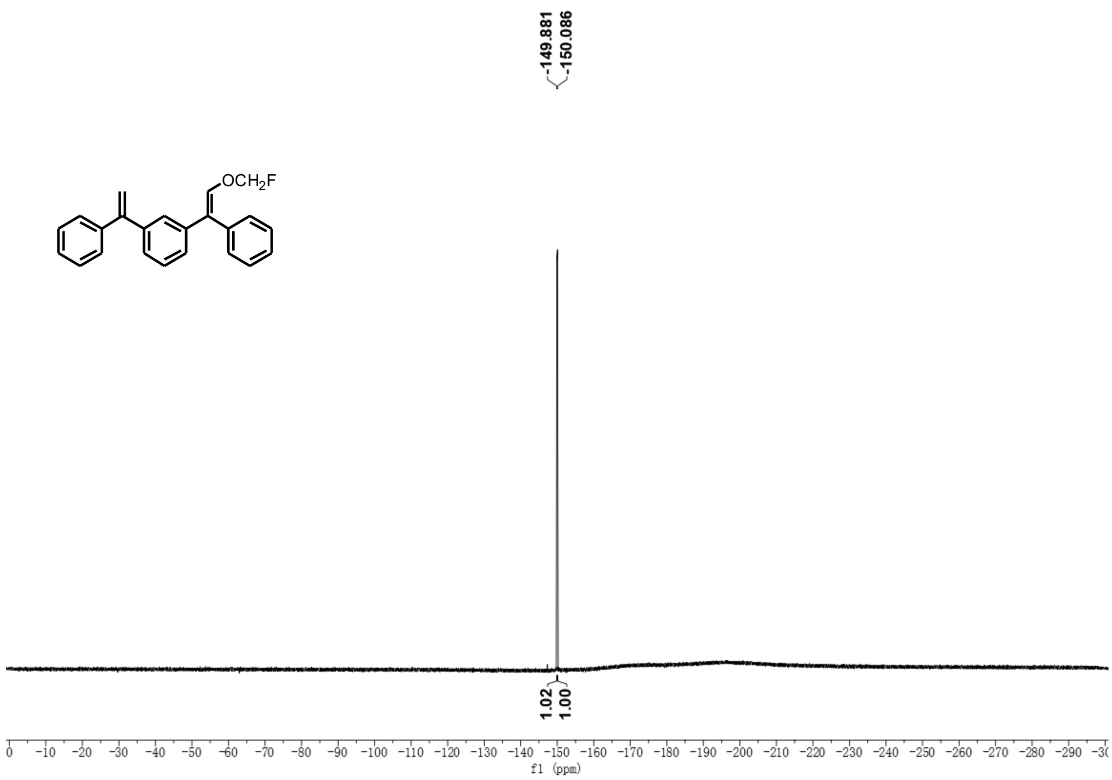
^{1}H NMR Spectrum of Compound **20** (400 MHz, $CDCl_3$)



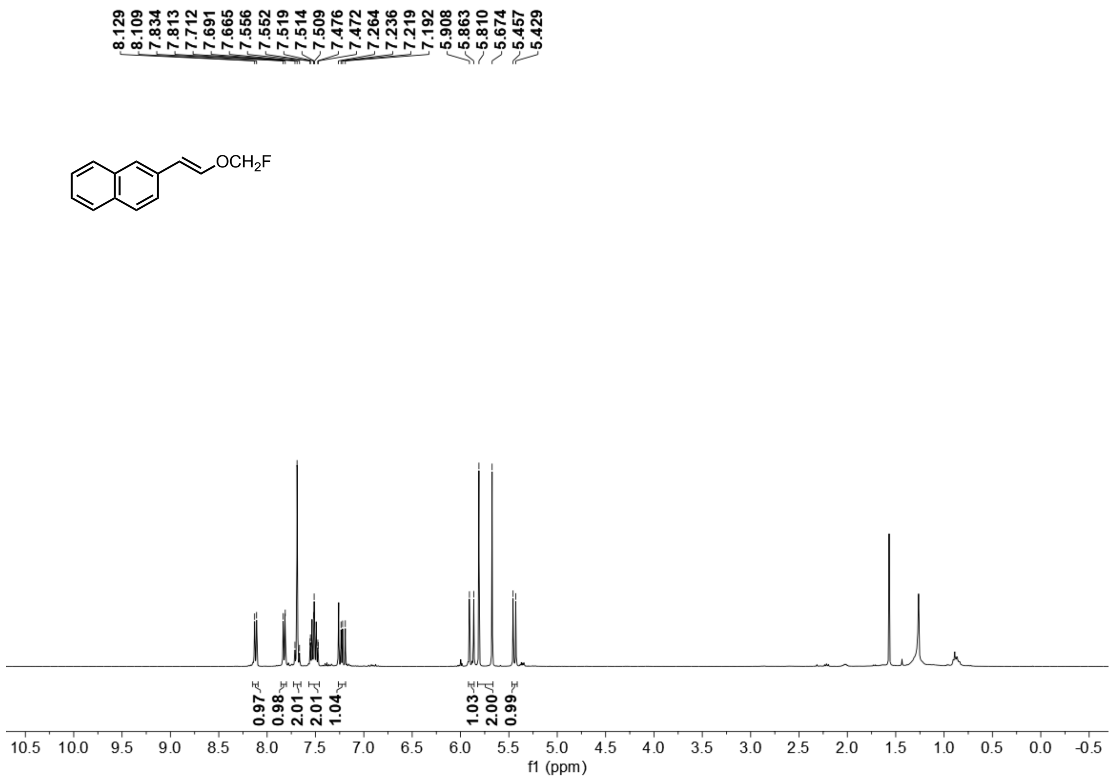
^{13}C NMR Spectrum of Compound **20** (151 MHz, $CDCl_3$)



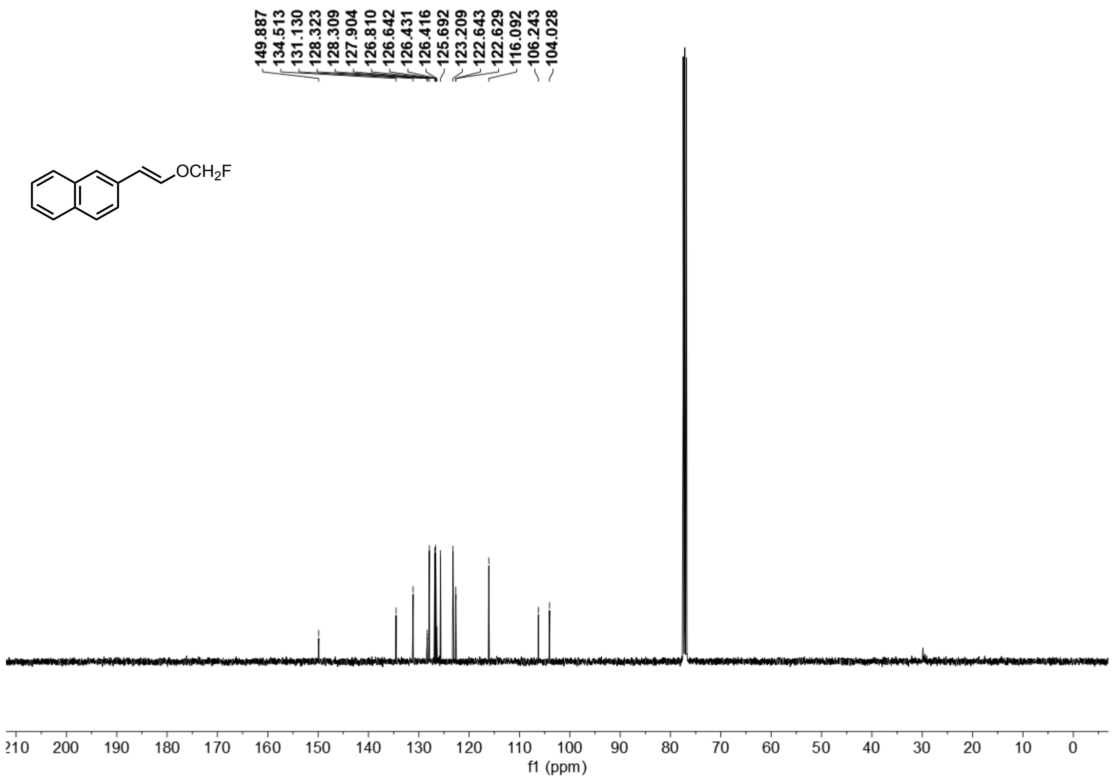
^{19}F NMR Spectrum of Compound **20** (376 MHz, $CDCl_3$)



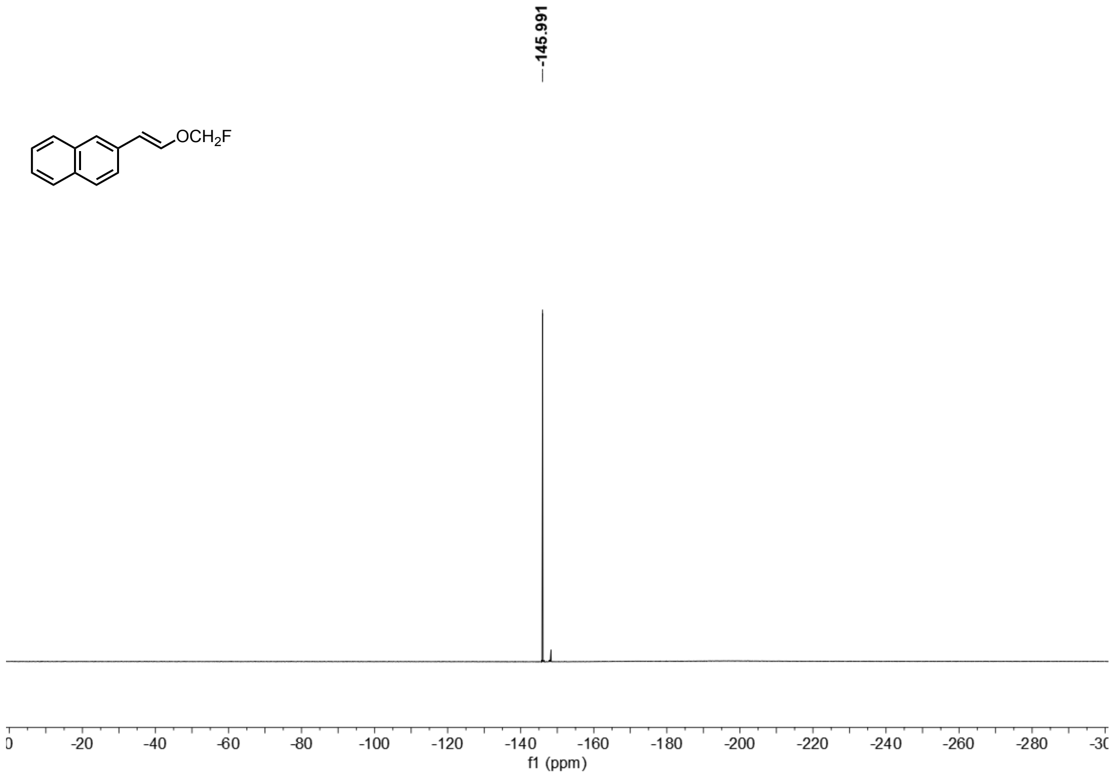
[1]H NMR Spectrum of Compound **21** (400 MHz, $CDCl_3$)



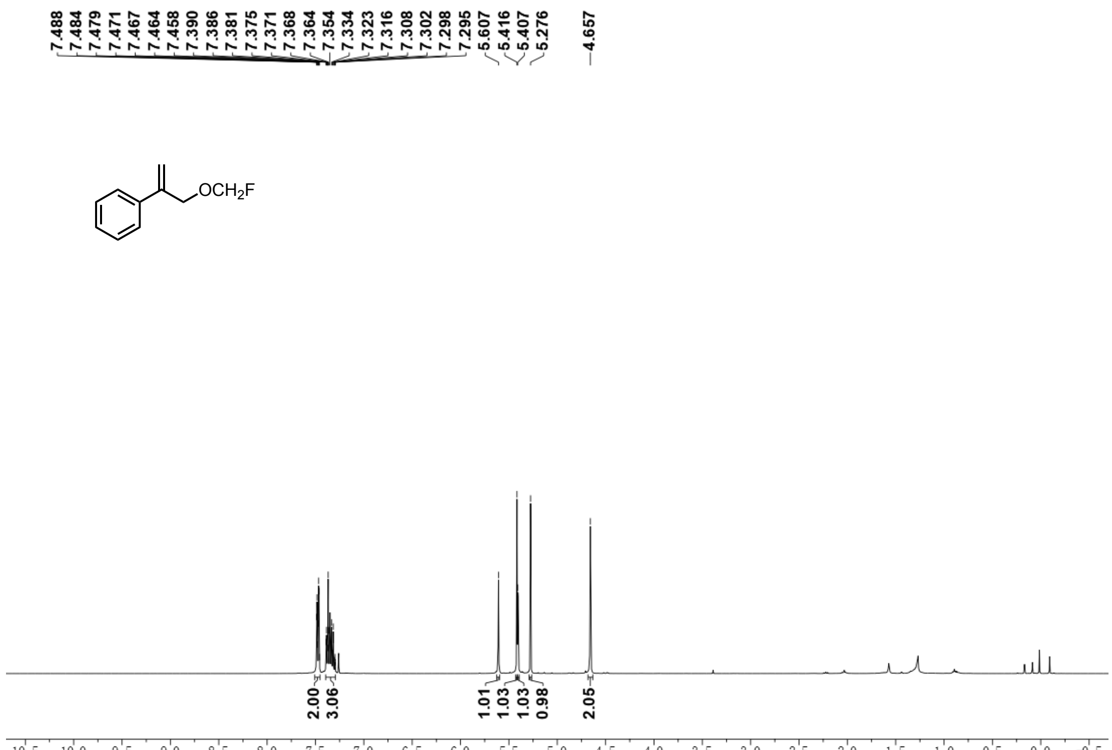
[13]C NMR Spectrum of Compound **21** (101 MHz, $CDCl_3$)



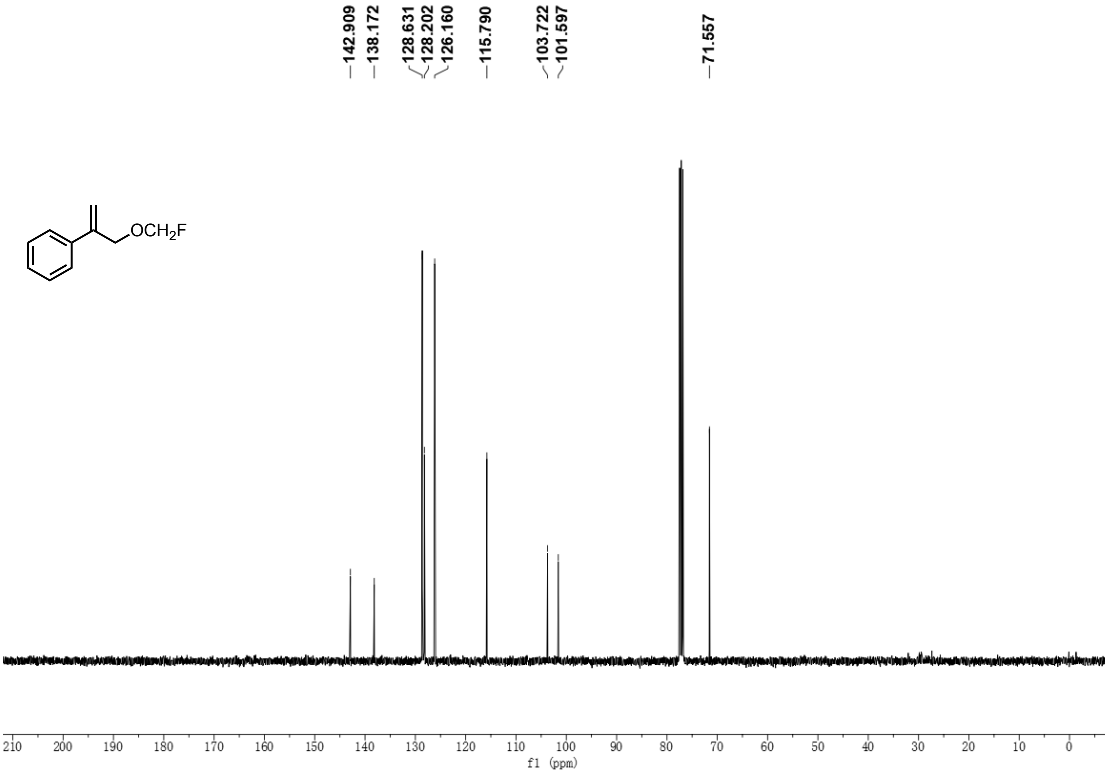
^{19}F NMR Spectrum of Compound **21** (376 MHz, $CDCl_3$)



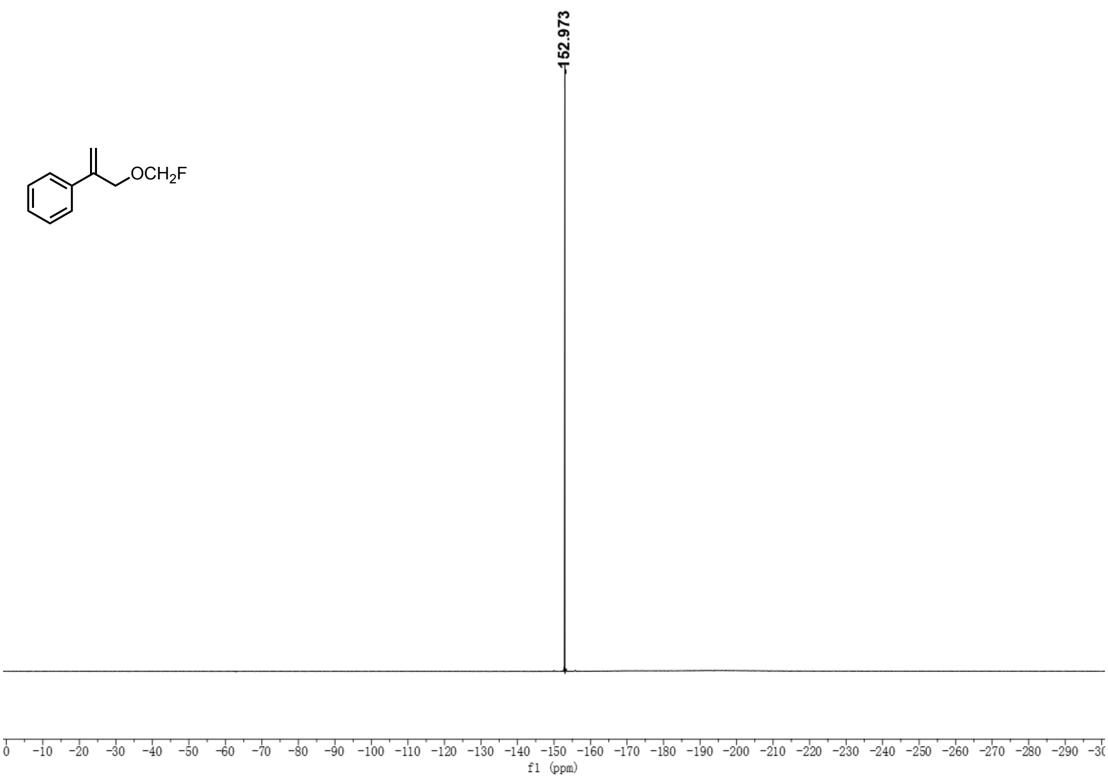
^{1}H NMR Spectrum of Compound **22** (400 MHz, $CDCl_3$)



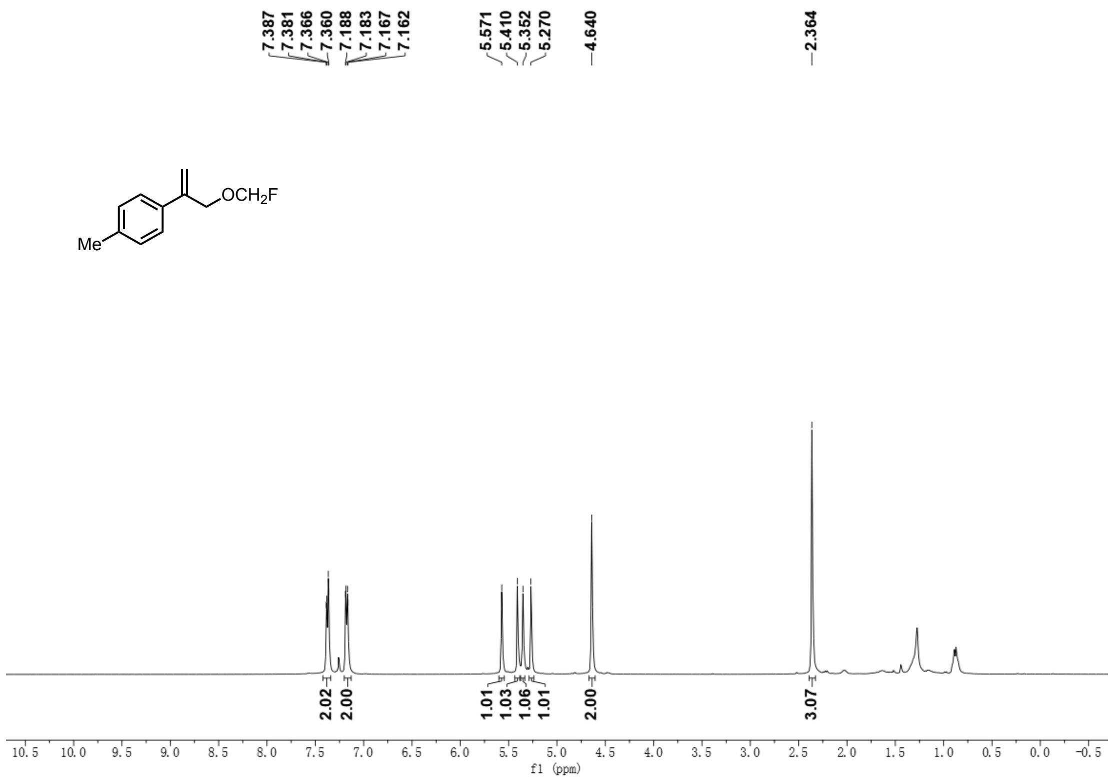
^{13}C NMR Spectrum of Compound **22** (101 MHz, $CDCl_3$)



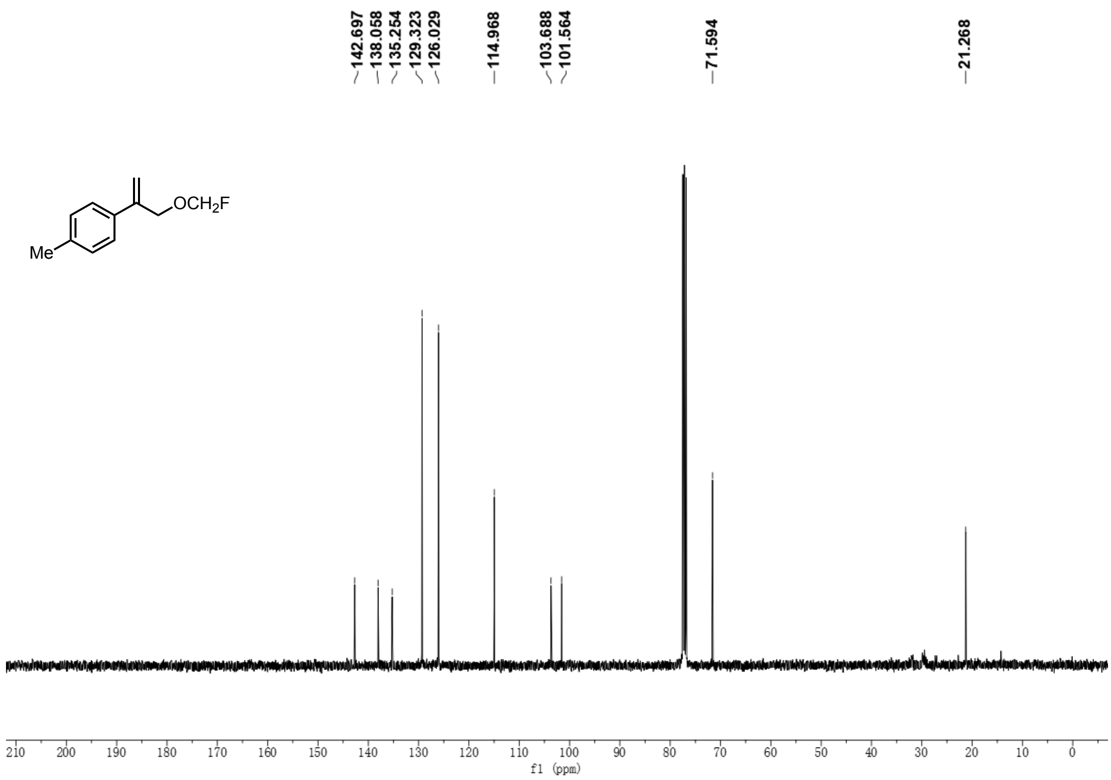
^{19}F NMR Spectrum of Compound **22** (376 MHz, $CDCl_3$)



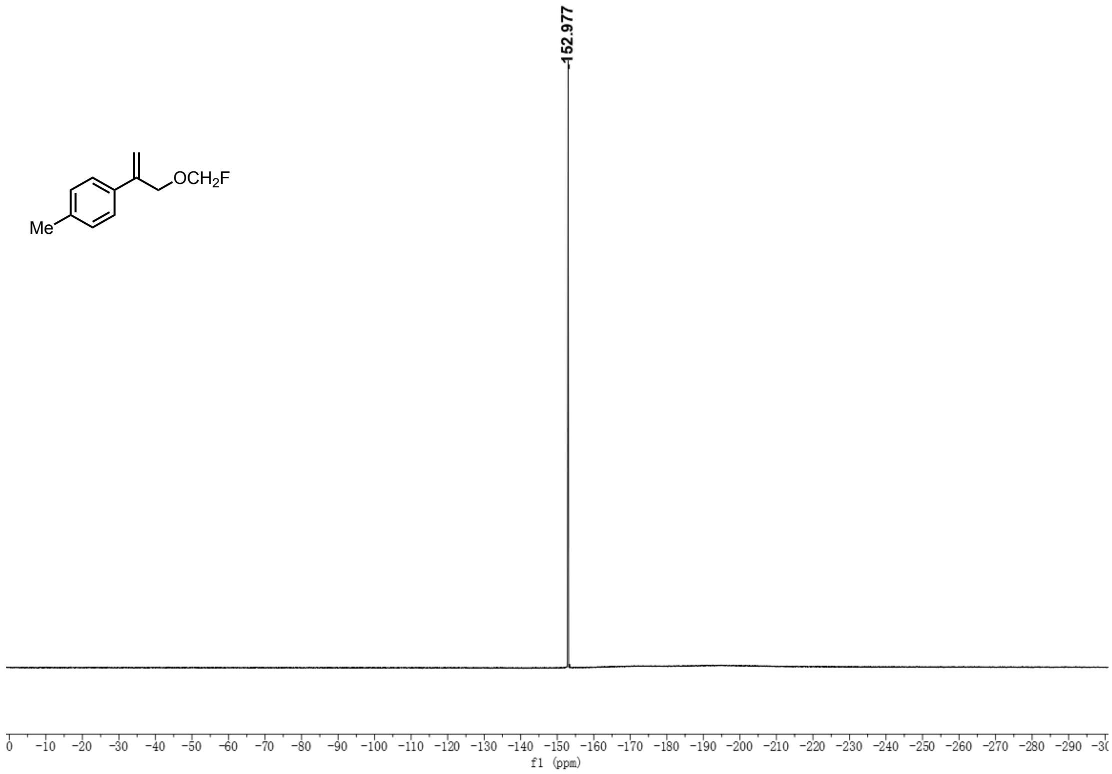
[1]H NMR Spectrum of Compound **23** (400 MHz, $CDCl_3$)



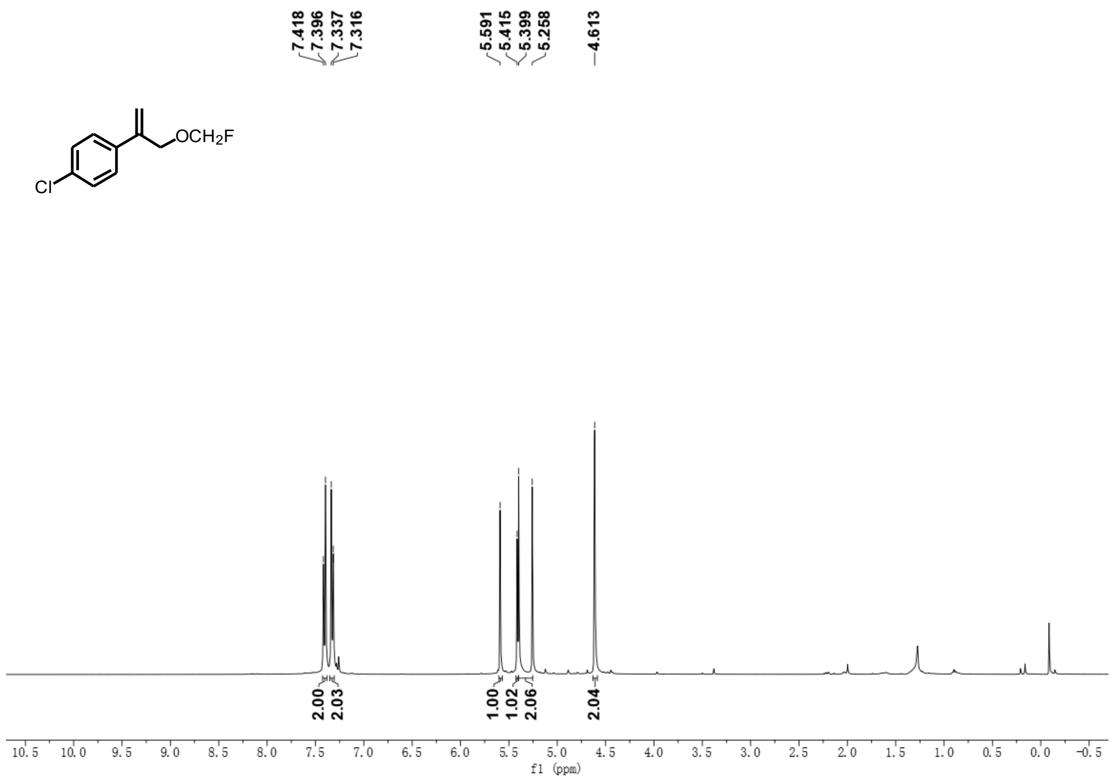
[13]C NMR Spectrum of Compound **23** (101 MHz, $CDCl_3$)



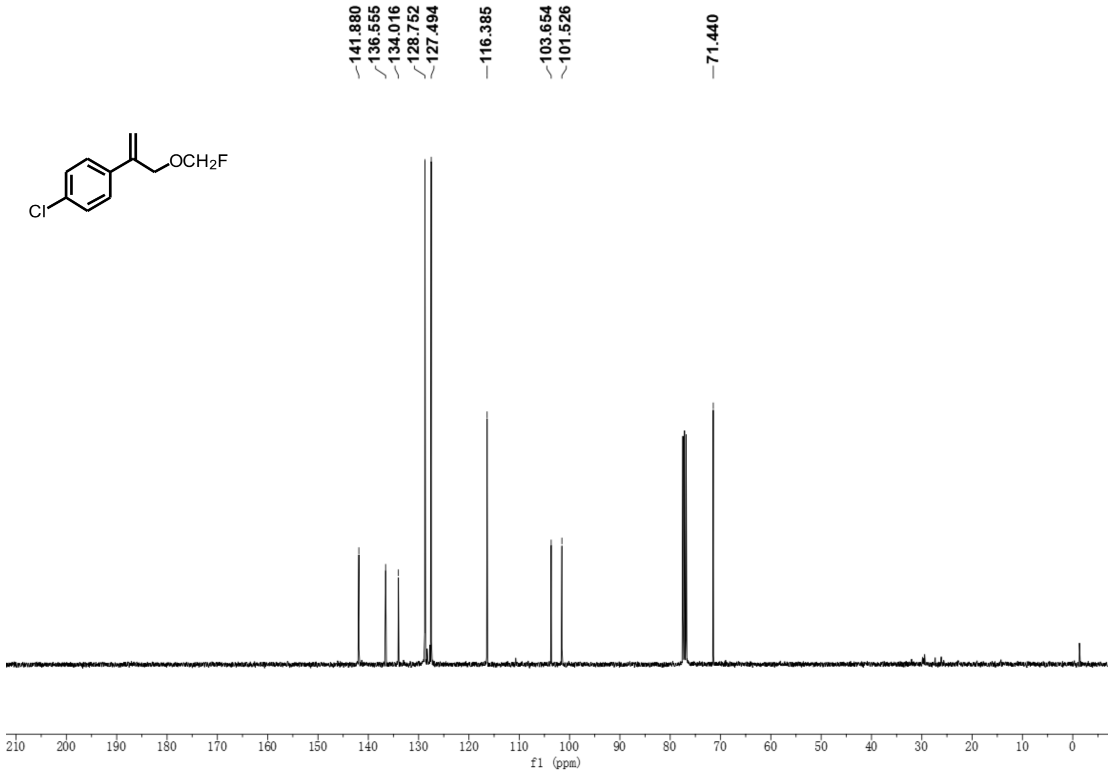
^{19}F NMR Spectrum of Compound **23** (376 MHz, $CDCl_3$)



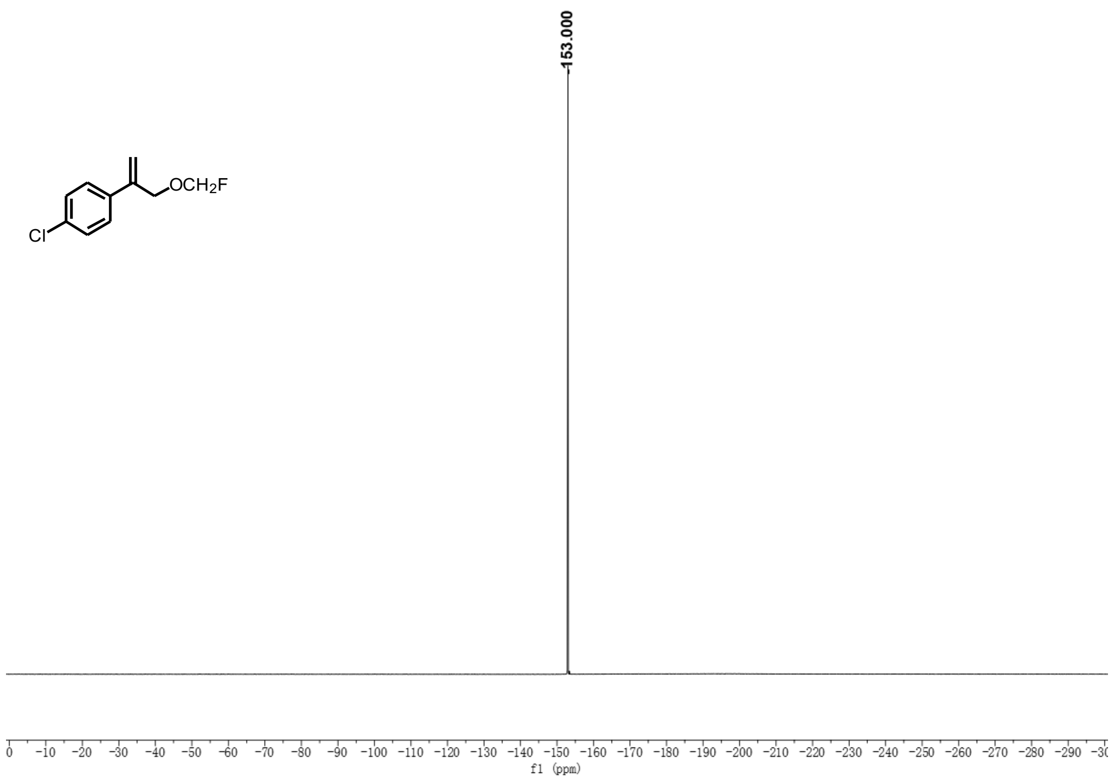
^{1}H NMR Spectrum of Compound **24** (400 MHz, $CDCl_3$)



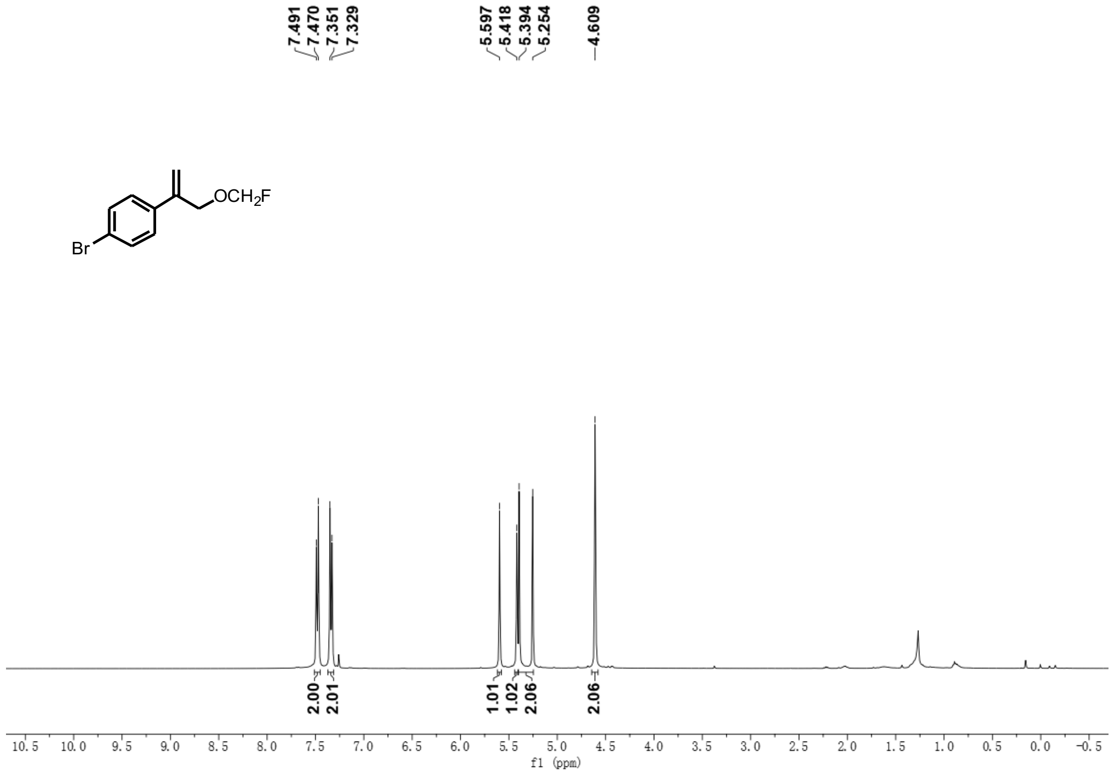
^{13}C NMR Spectrum of Compound **24** (101 MHz, CDCl$_3$)



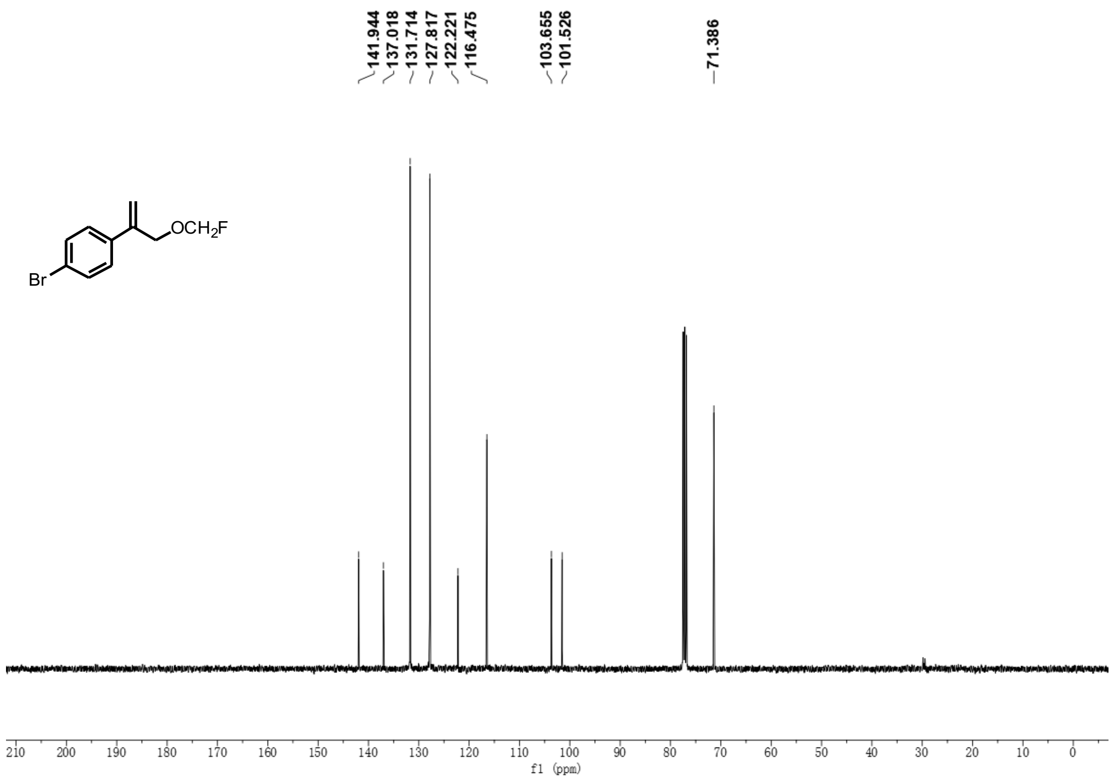
^{19}F NMR Spectrum of Compound **24** (376 MHz, CDCl$_3$)



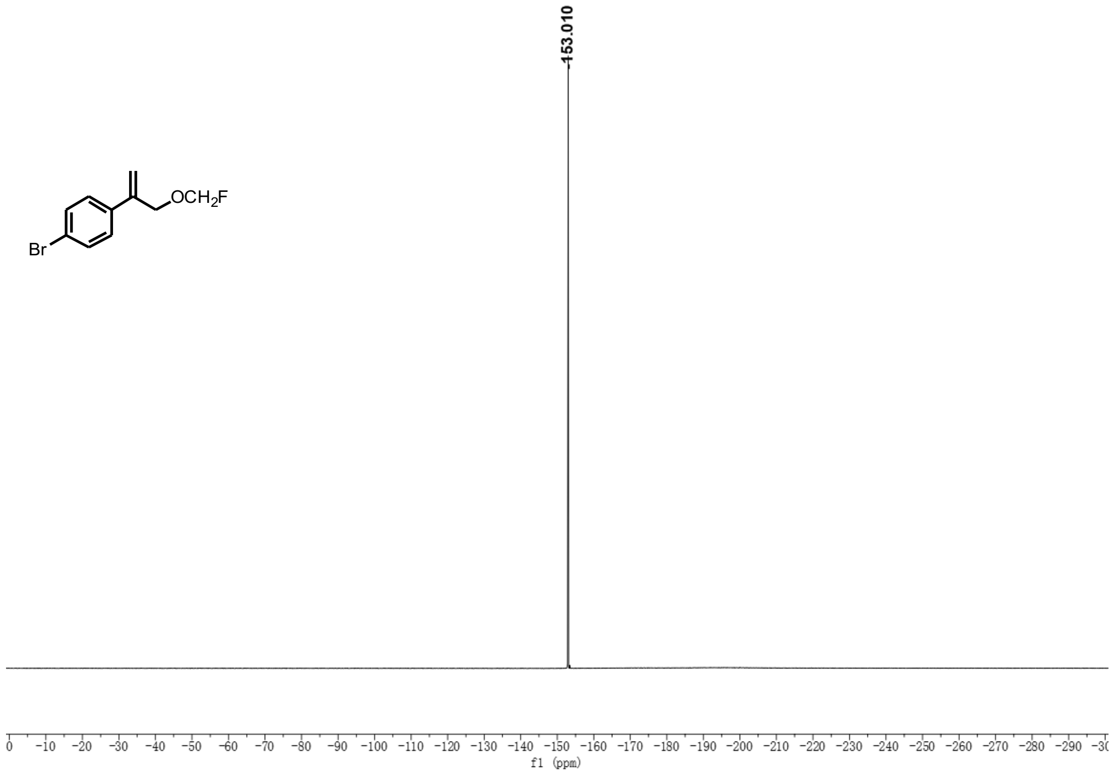
[1]H NMR Spectrum of Compound **25** (400 MHz, $CDCl_3$)



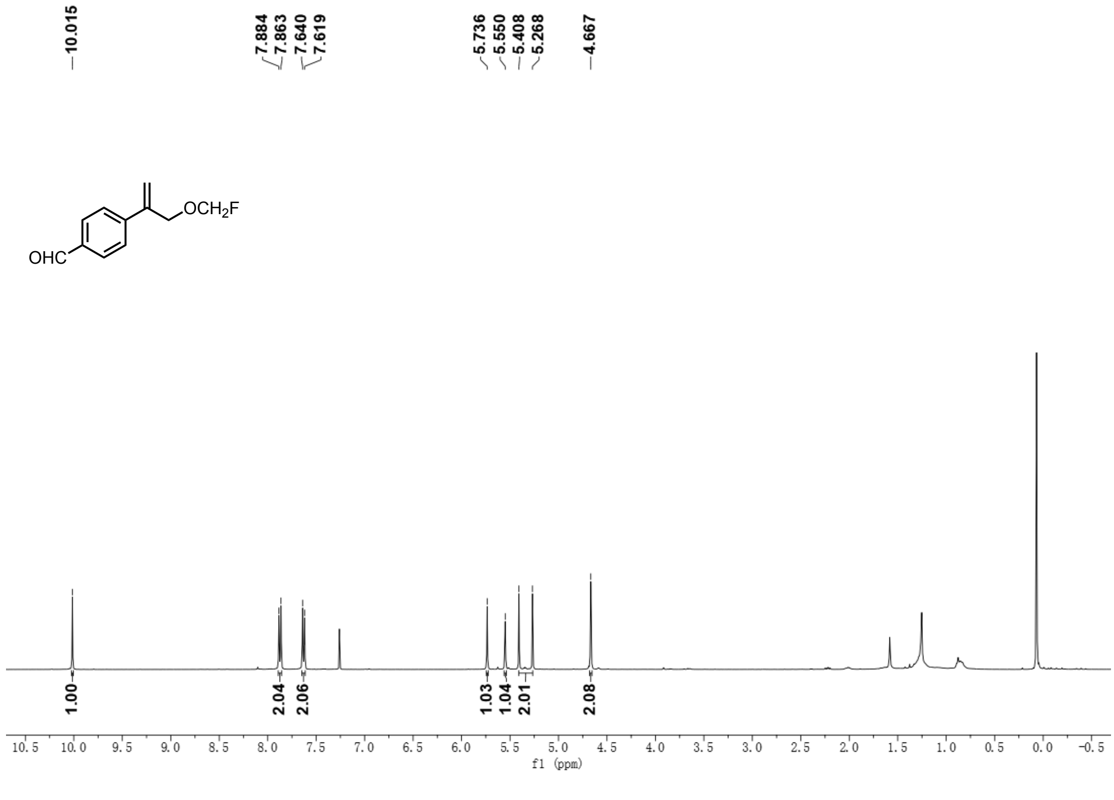
[13]C NMR Spectrum of Compound **25** (101 MHz, $CDCl_3$)



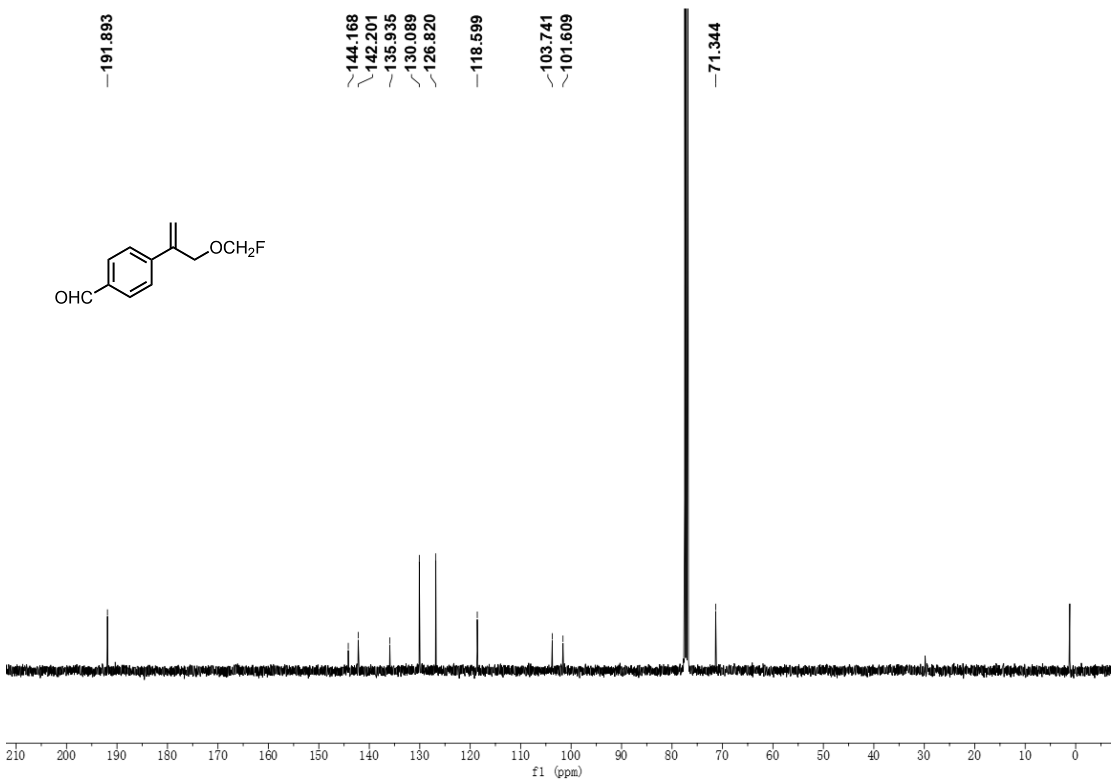
^{19}F NMR Spectrum of Compound **25** (376 MHz, $CDCl_3$)



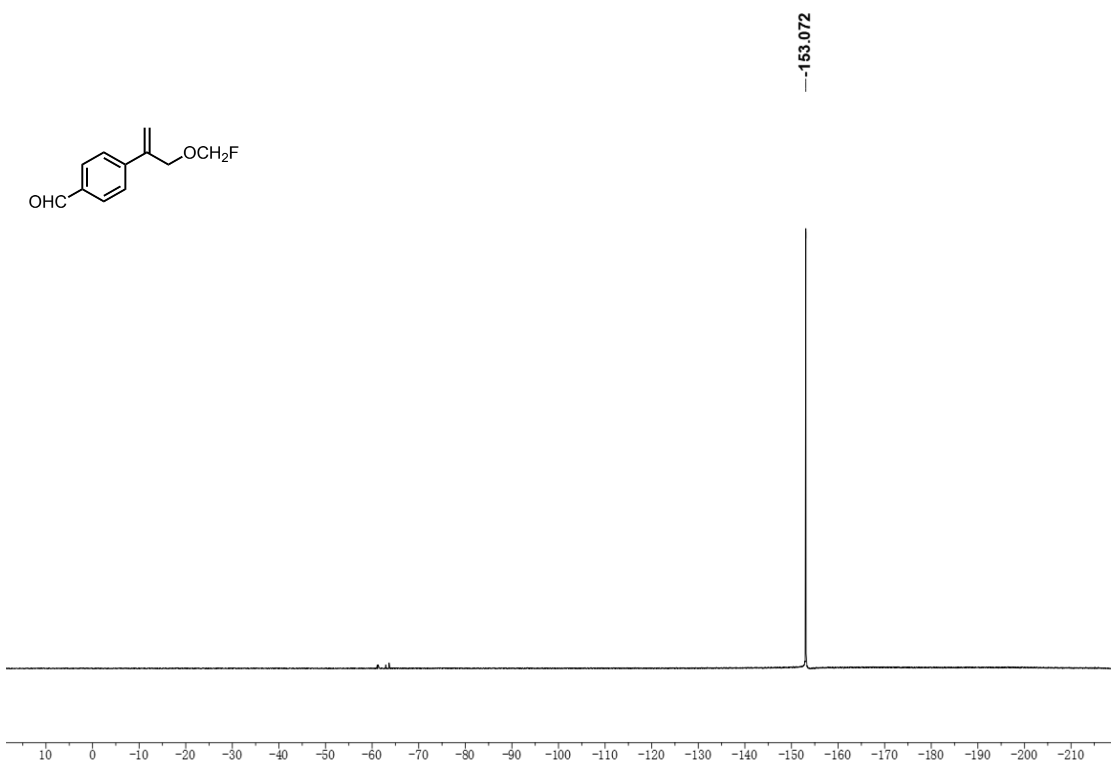
^{1}H NMR Spectrum of Compound **26** (400 MHz, $CDCl_3$)



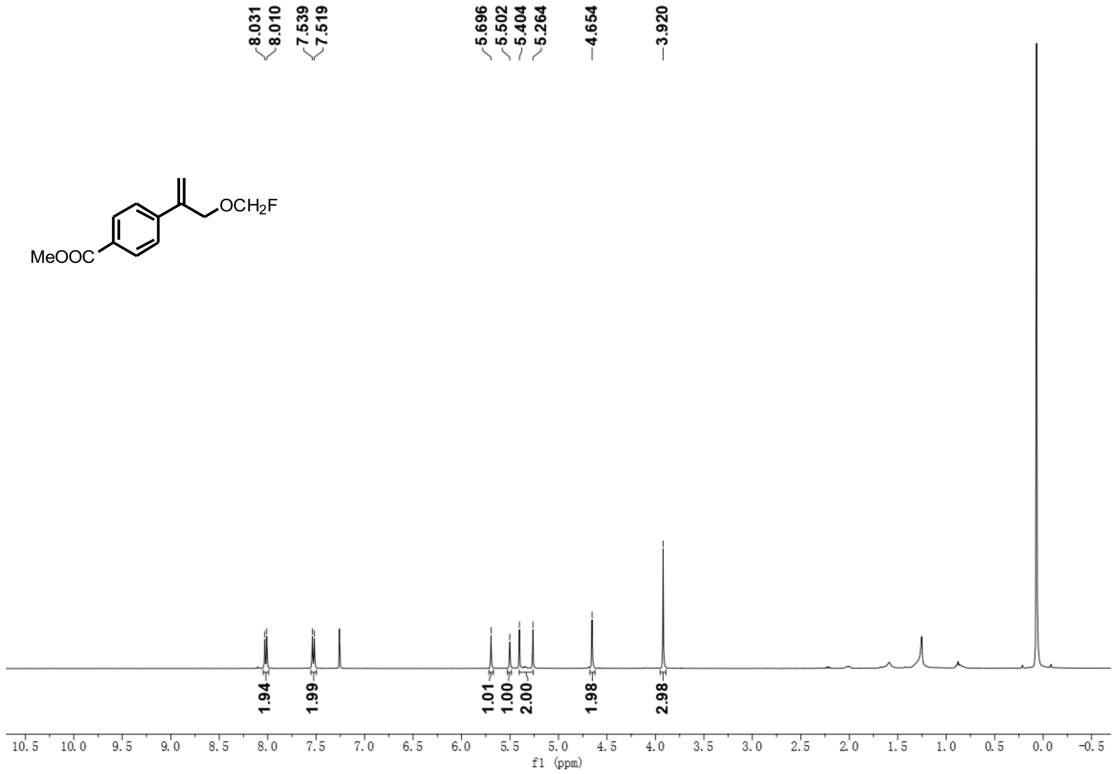
^{13}C NMR Spectrum of Compound **26** (101 MHz, $CDCl_3$)



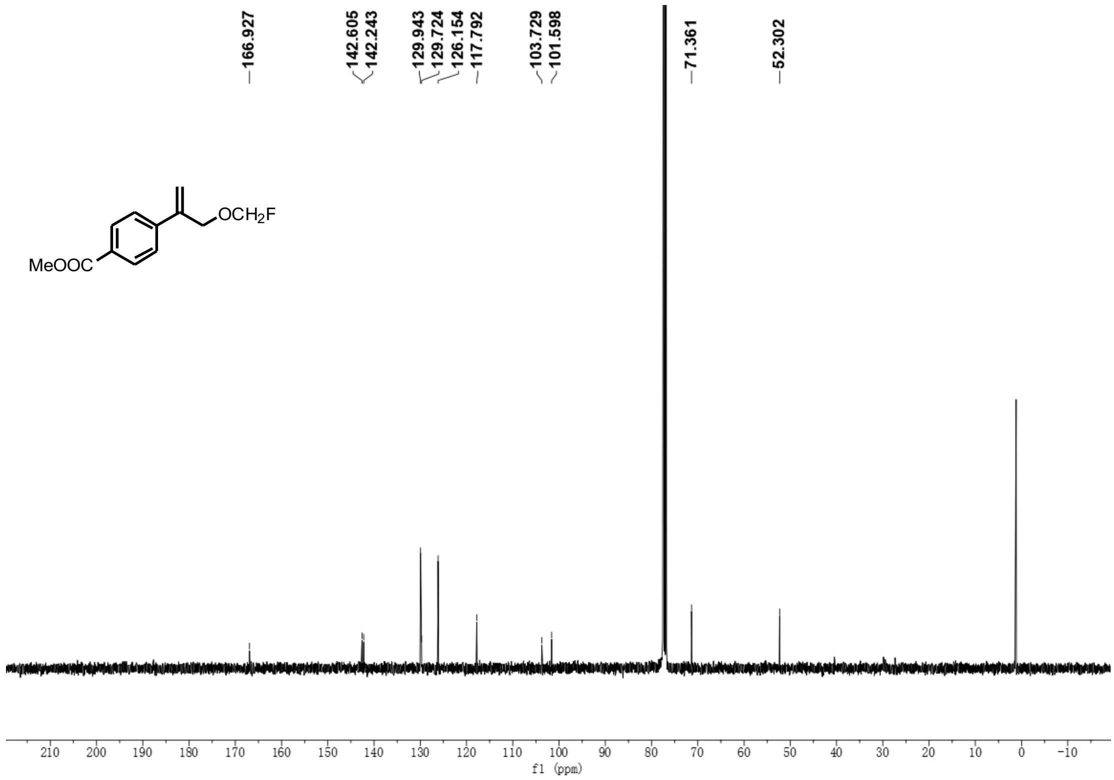
^{19}F NMR Spectrum of Compound **26** (376 MHz, $CDCl_3$)



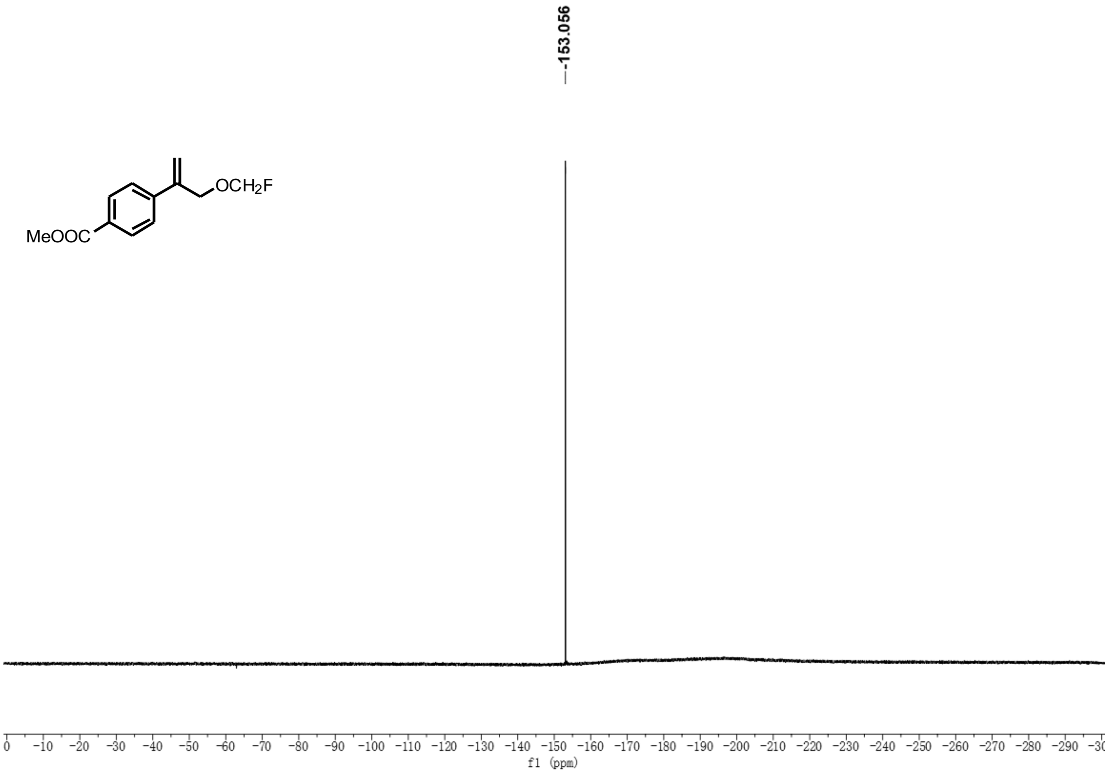
[1]H NMR Spectrum of Compound **27** (400 MHz, $CDCl_3$)



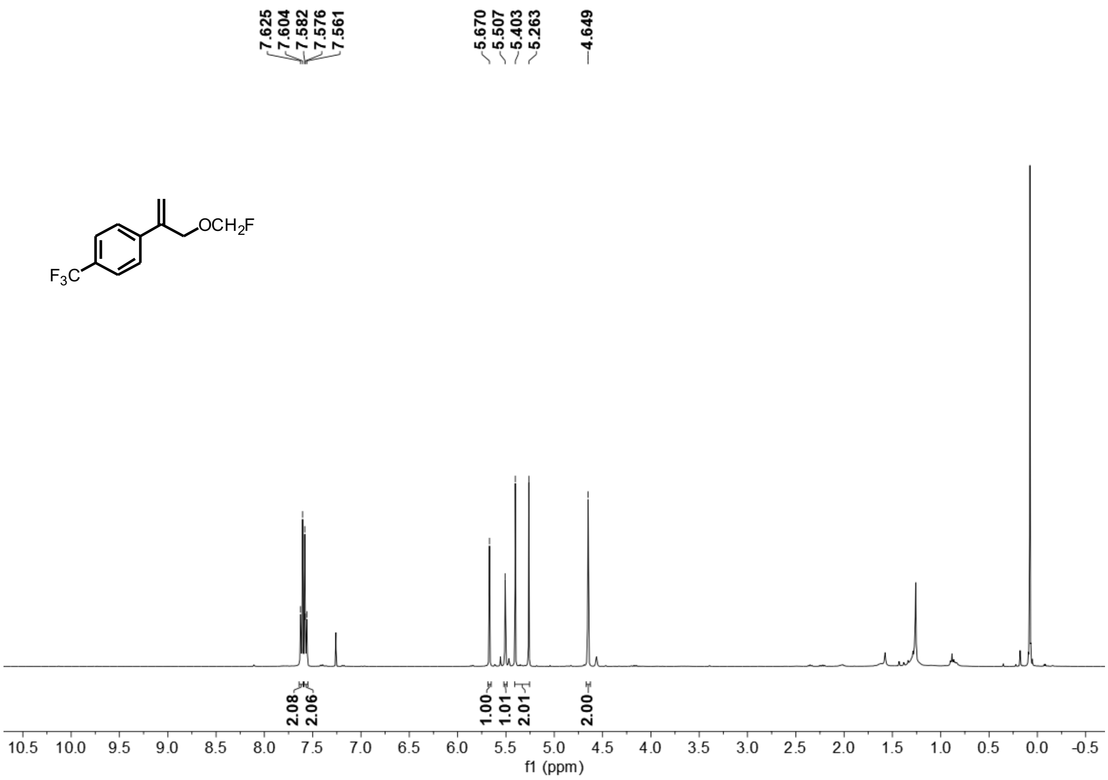
[13]C NMR Spectrum of Compound **27** (151 MHz, $CDCl_3$)



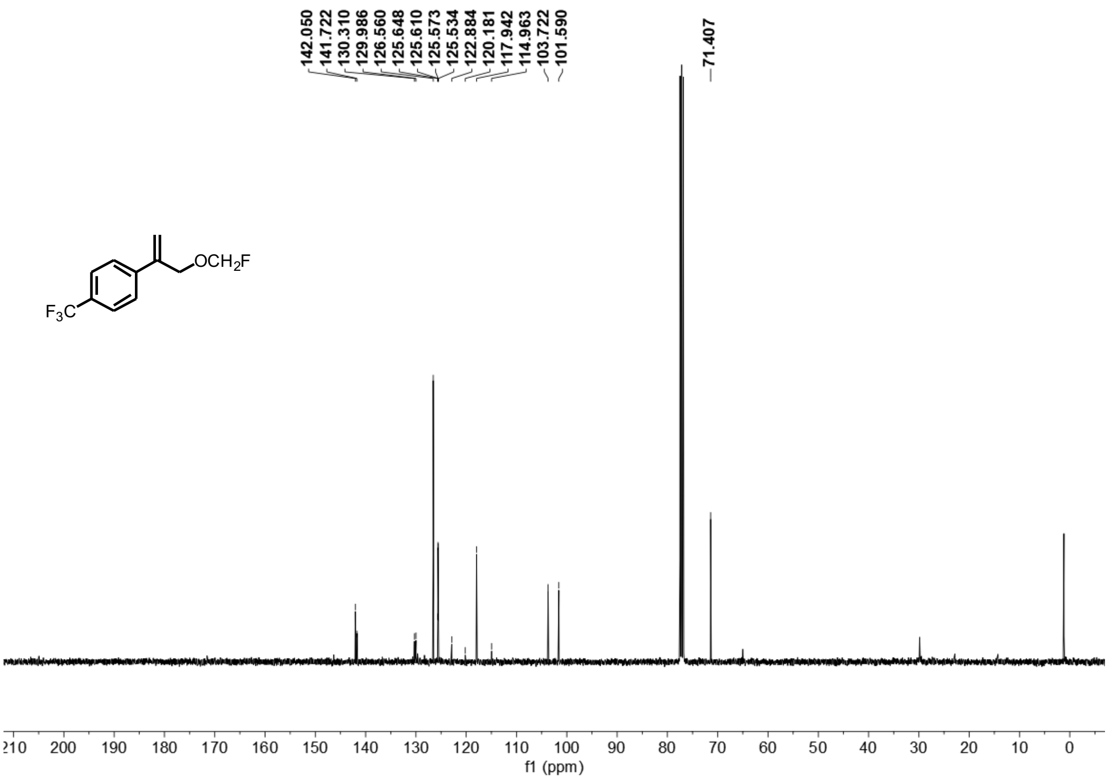
^{19}F NMR Spectrum of Compound **27** (376 MHz, $CDCl_3$)



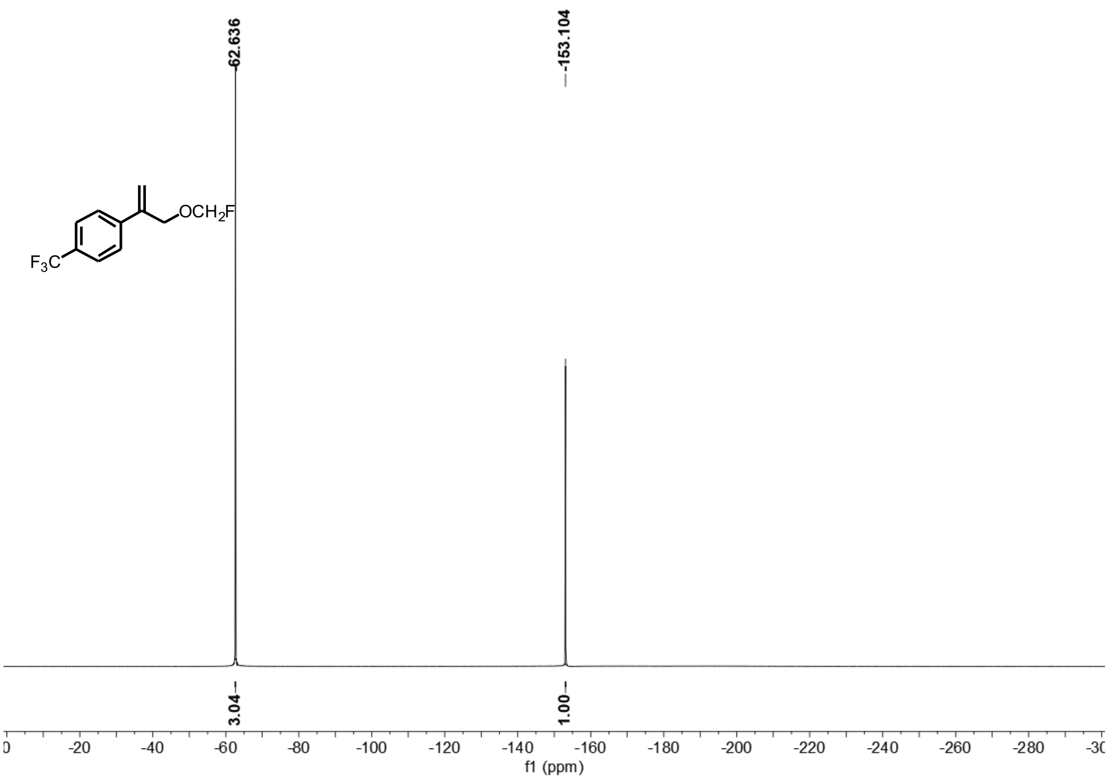
^{1}H NMR Spectrum of Compound **28** (400 MHz, $CDCl_3$)



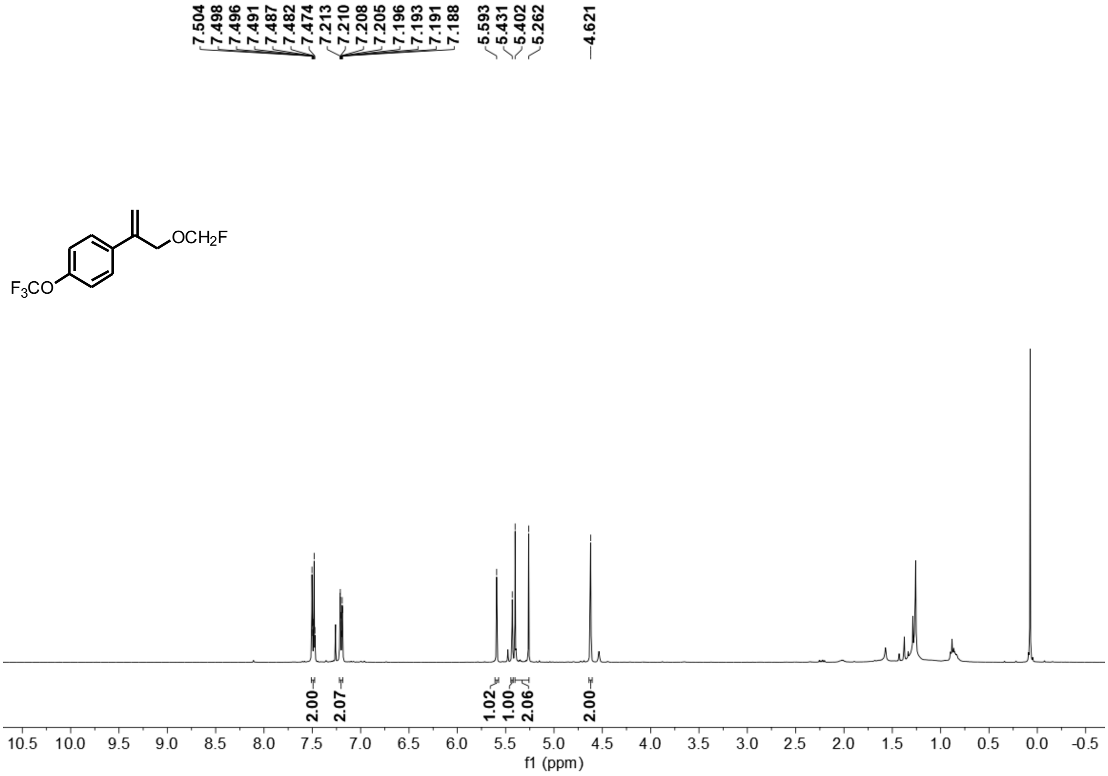
^{13}C NMR Spectrum of Compound **28** (101 MHz, $CDCl_3$)



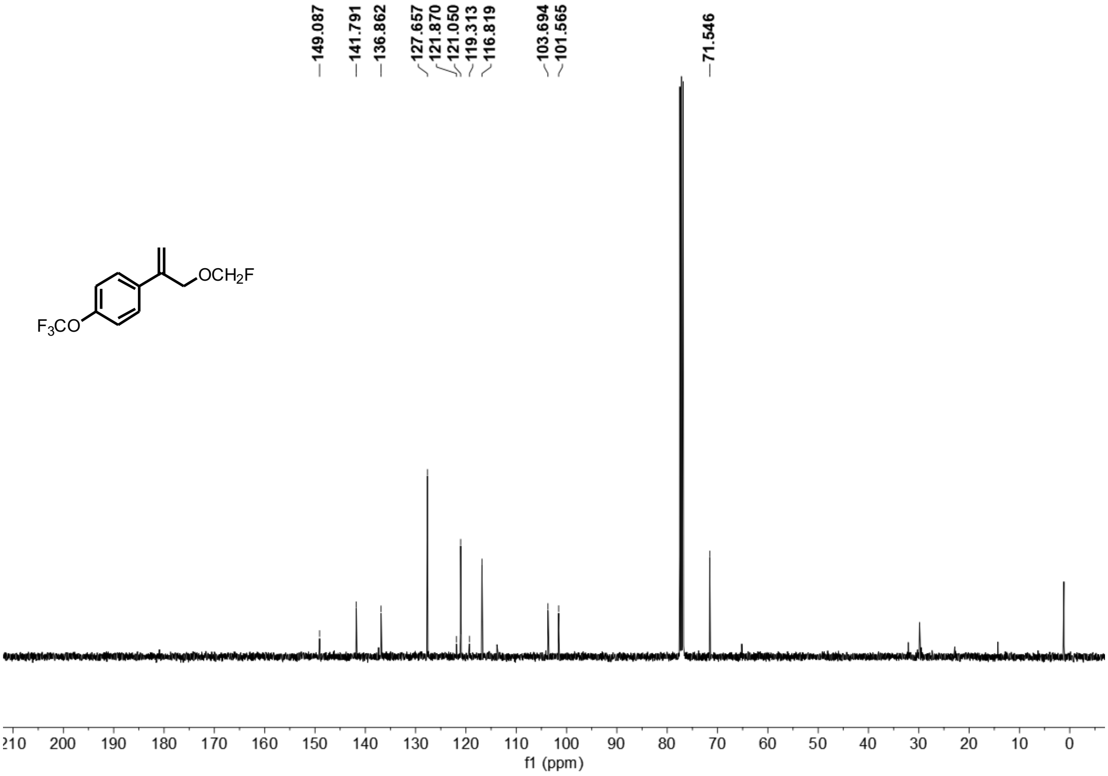
^{19}F NMR Spectrum of Compound **28** (376 MHz, $CDCl_3$)



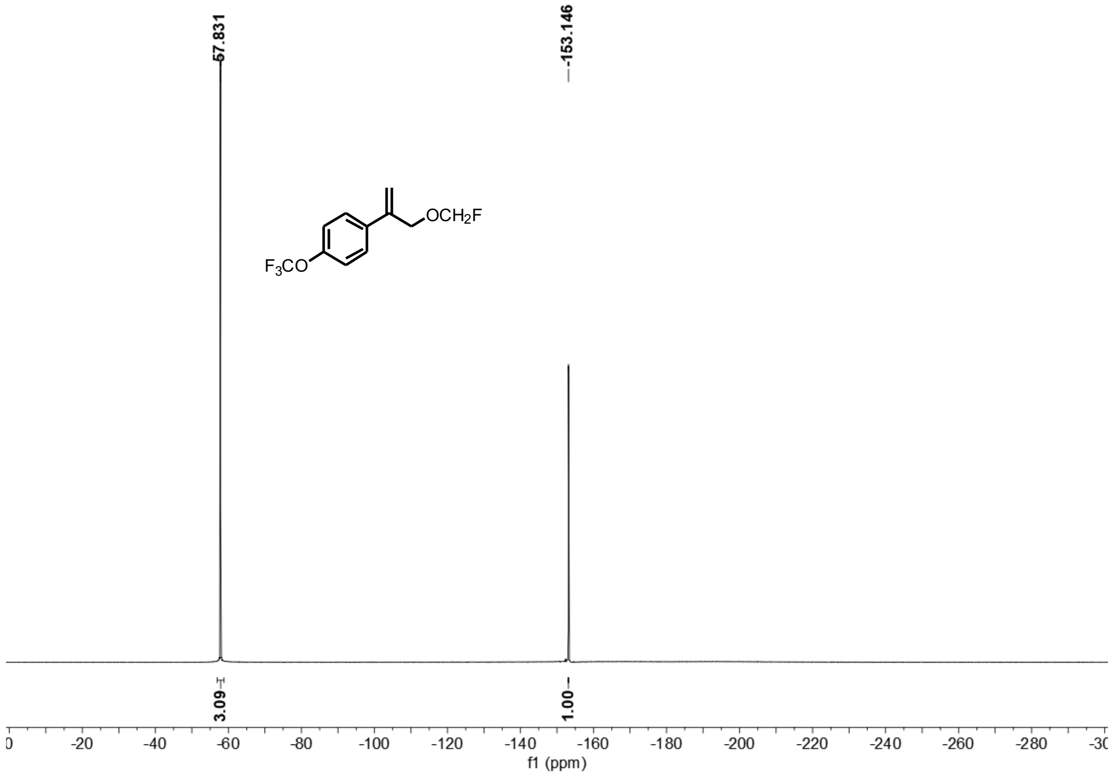
[1]H NMR Spectrum of Compound **29** (400 MHz, $CDCl_3$)



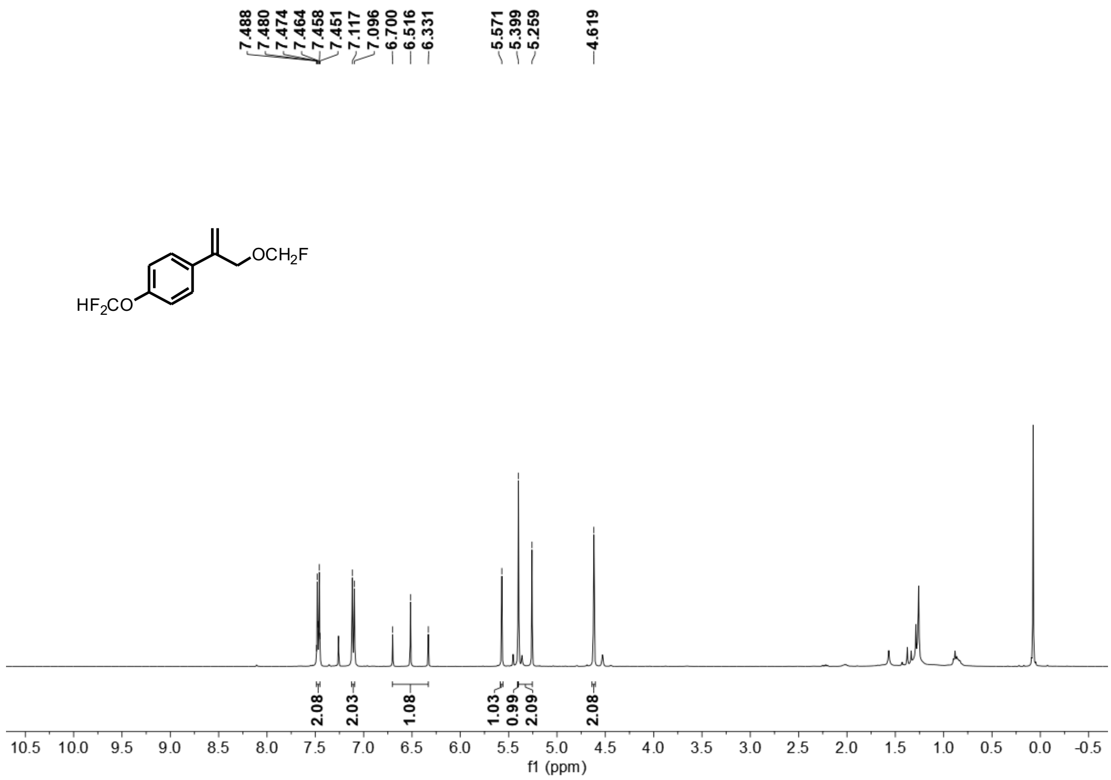
[13]C NMR Spectrum of Compound **29** (101 MHz, $CDCl_3$)



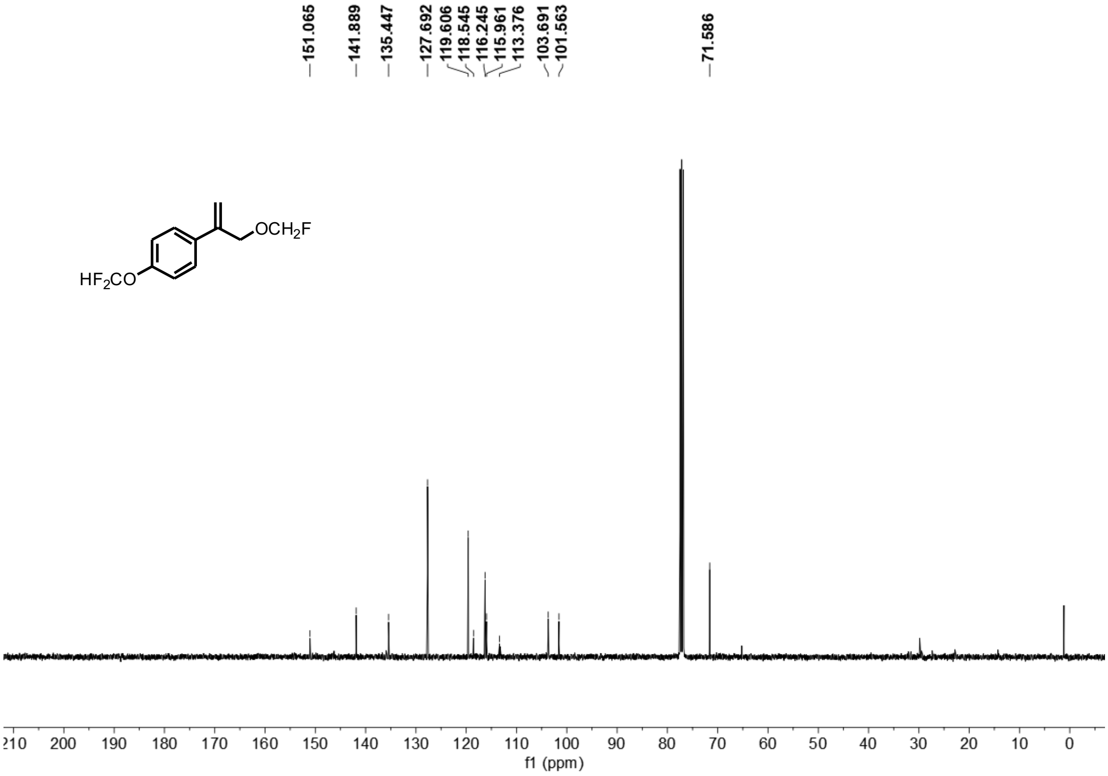
[19]F NMR Spectrum of Compound **29** (376 MHz, $CDCl_3$)



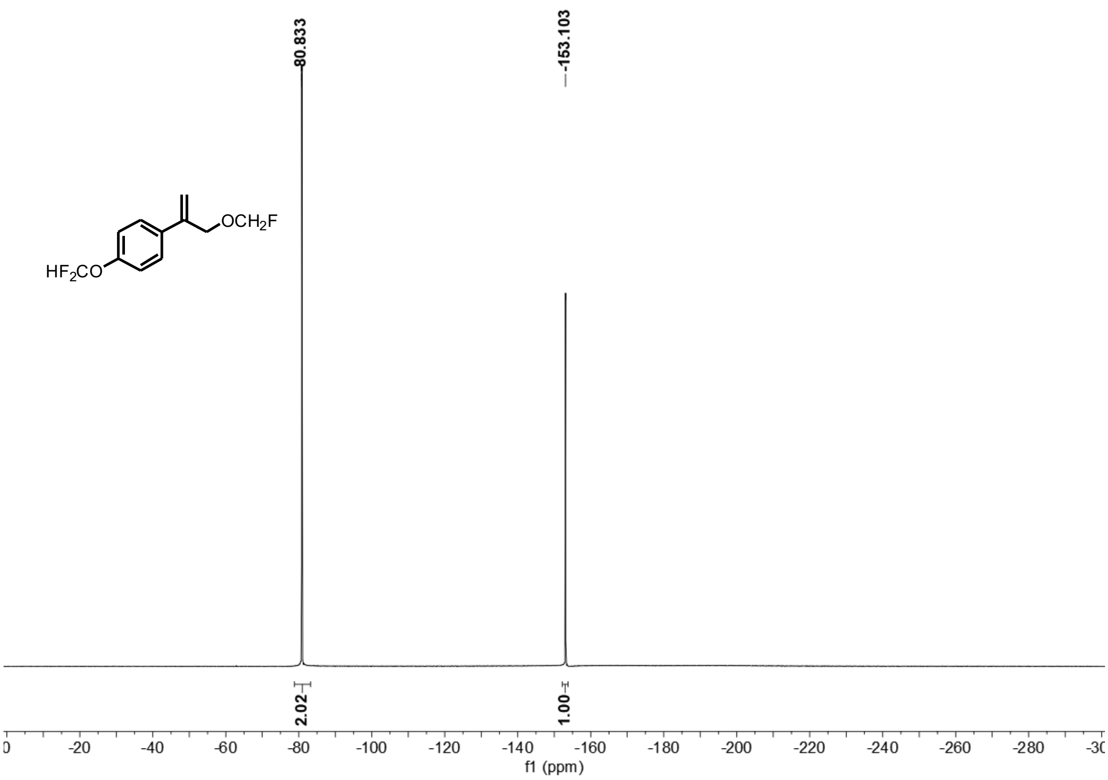
[1]H NMR Spectrum of Compound **30** (400 MHz, $CDCl_3$)



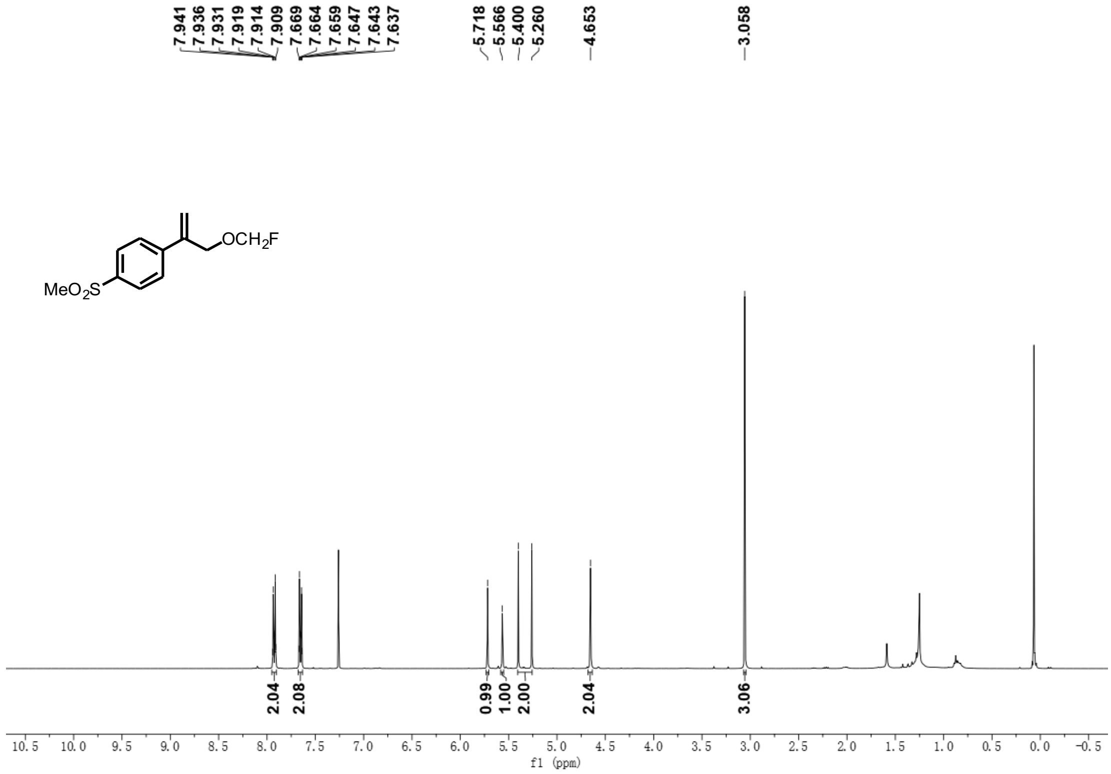
^{13}C NMR Spectrum of Compound **30** (101 MHz, $CDCl_3$)



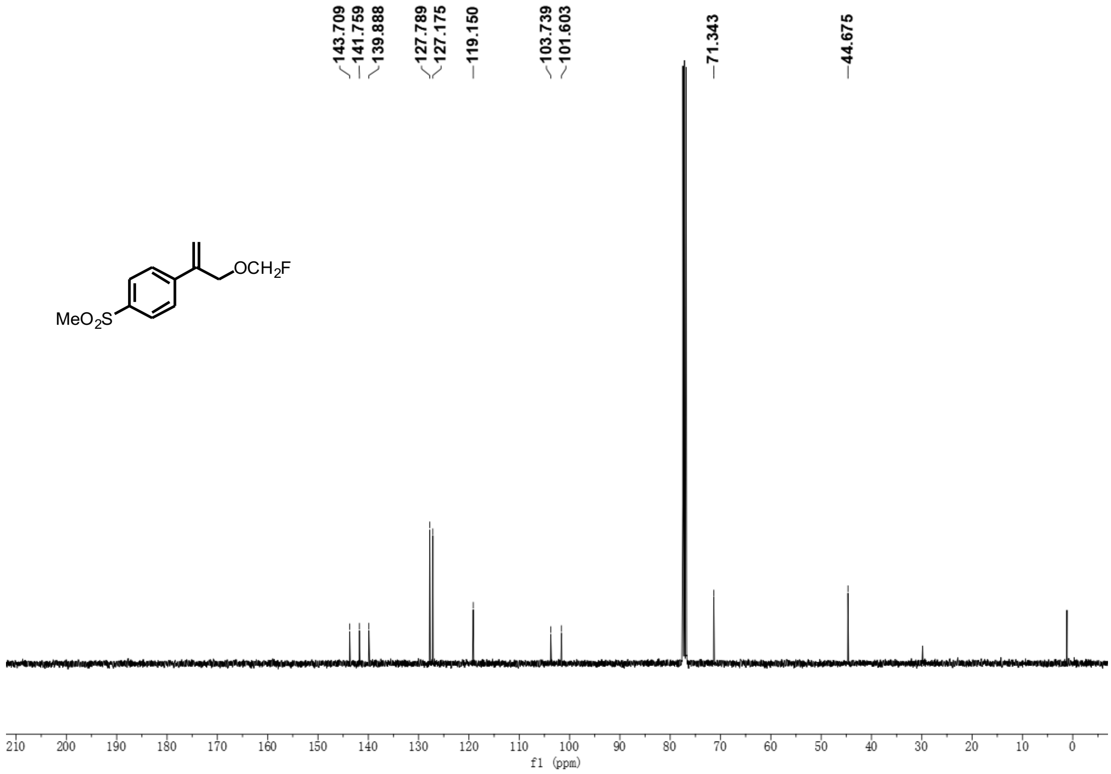
^{19}F NMR Spectrum of Compound **30** (376 MHz, $CDCl_3$)



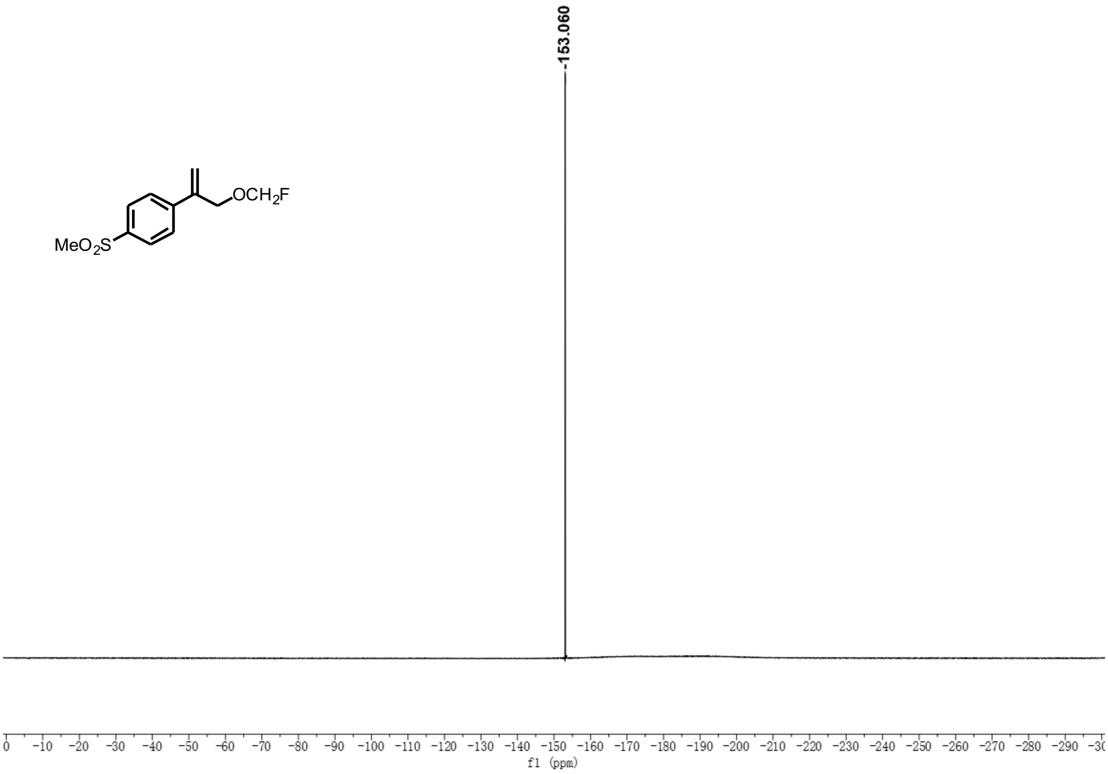
[1]H NMR Spectrum of Compound **31** (400 MHz, $CDCl_3$)



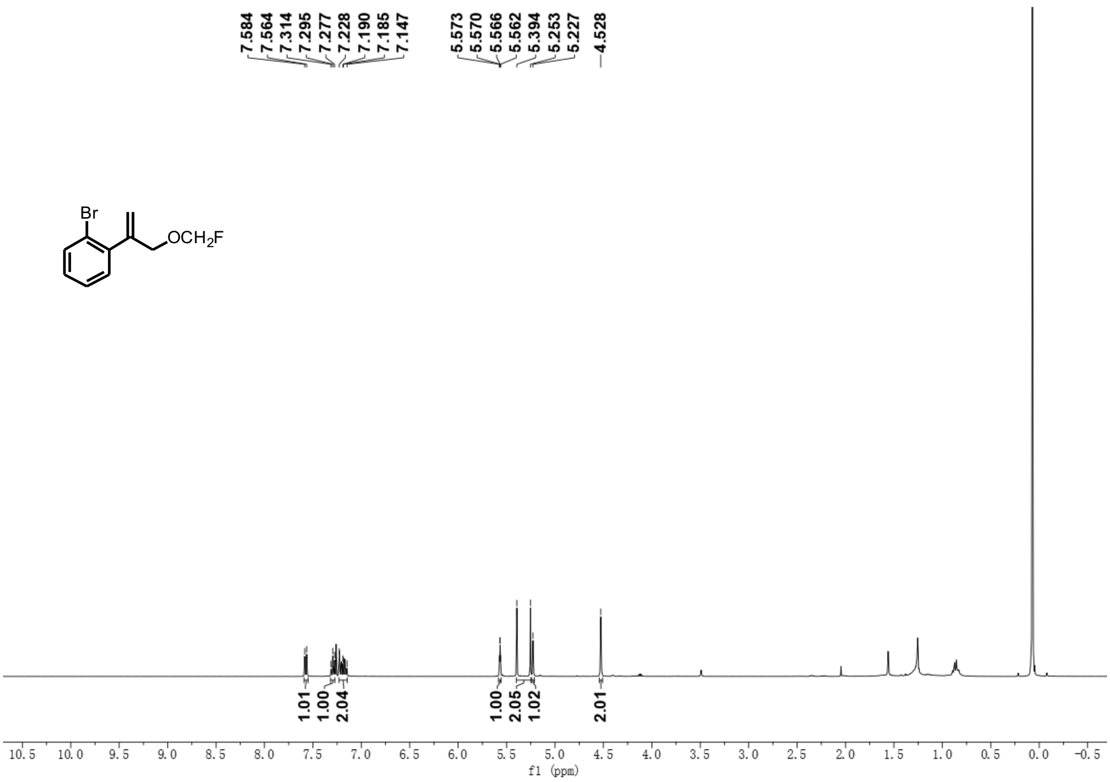
[13]C NMR Spectrum of Compound **31** (101 MHz, $CDCl_3$)



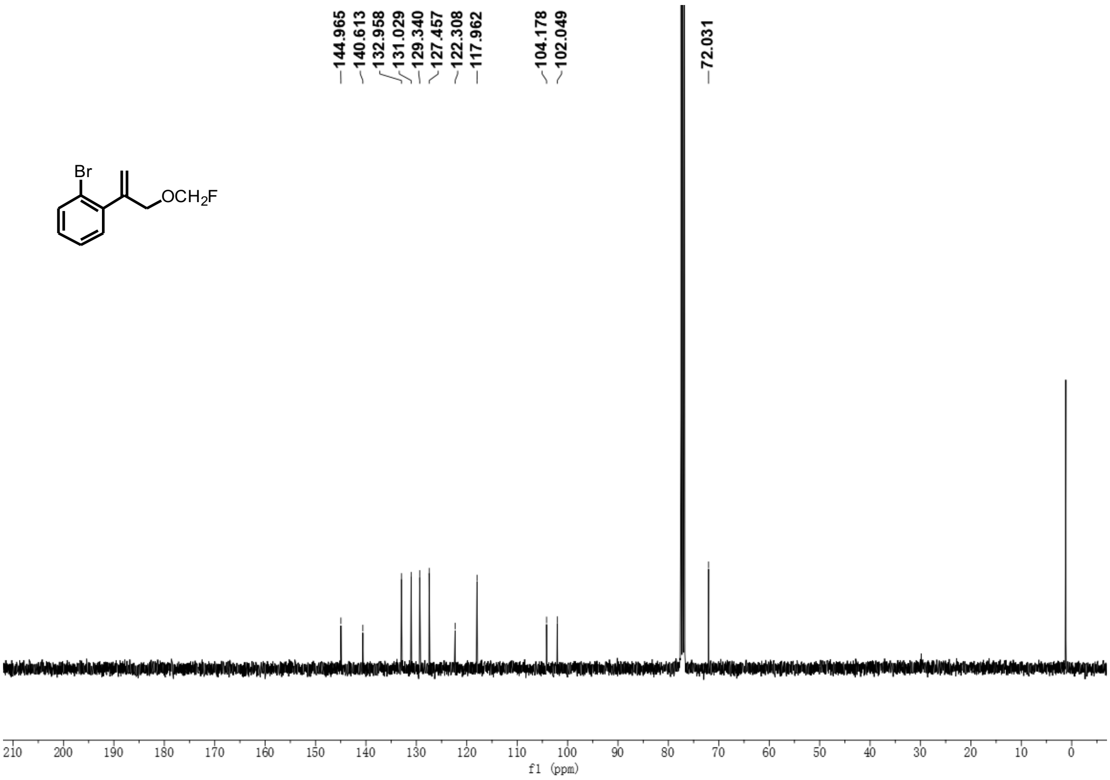
^{19}F NMR Spectrum of Compound **31** (376 MHz, $CDCl_3$)



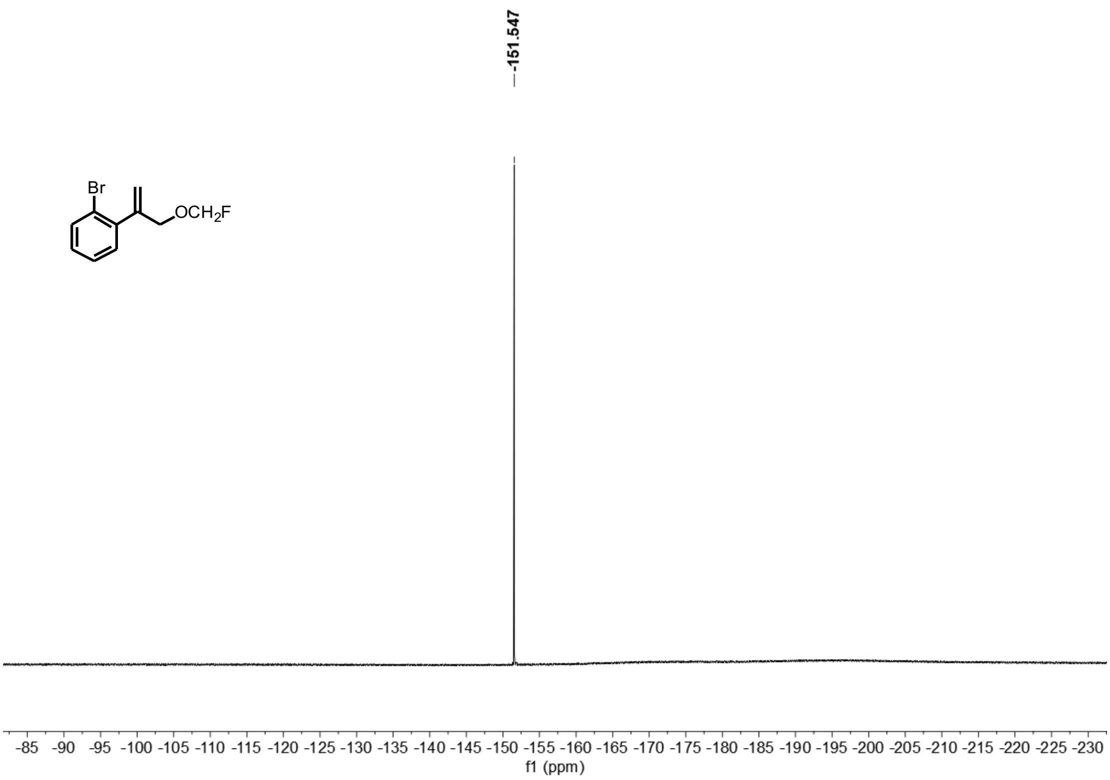
^{1}H NMR Spectrum of Compound **32** (400 MHz, $CDCl_3$)



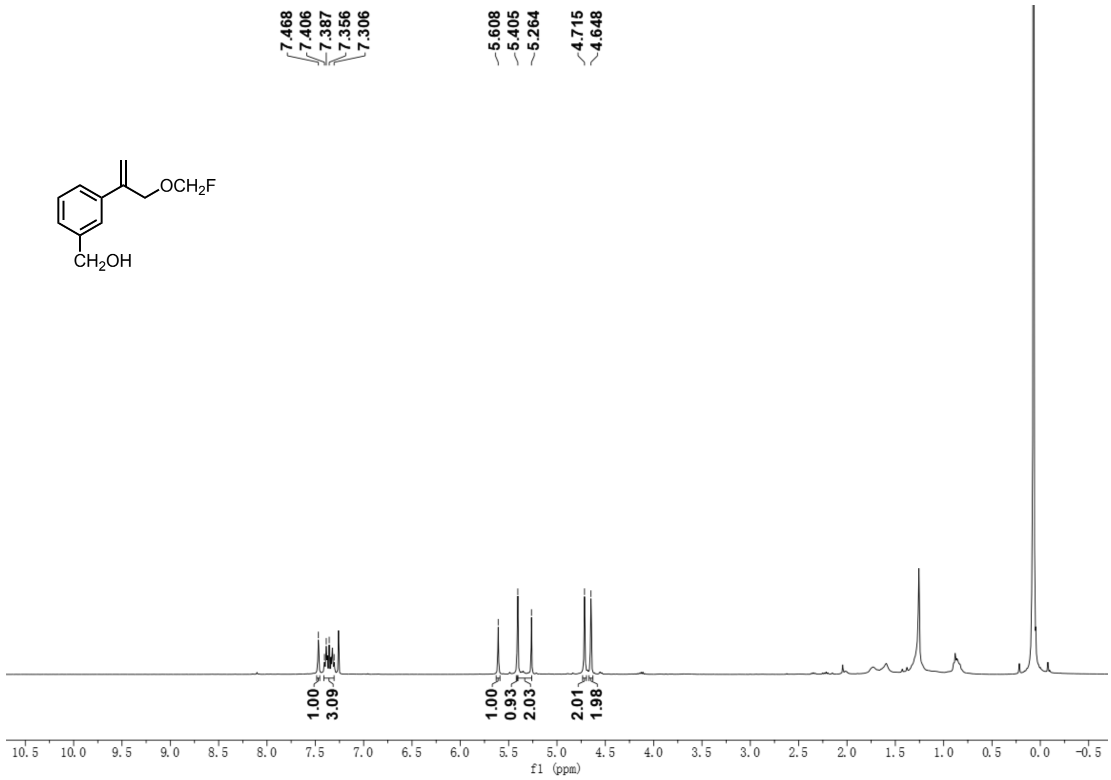
^{13}C NMR Spectrum of Compound **32** (101 MHz, $CDCl_3$)



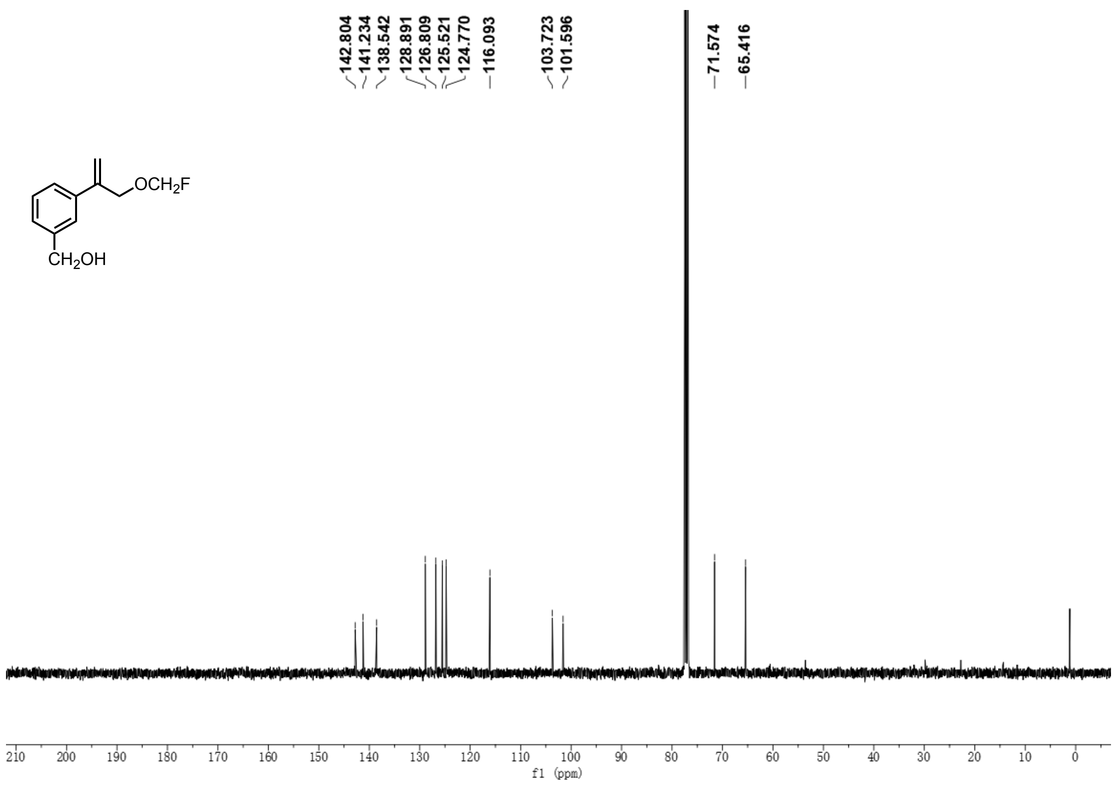
^{19}F NMR Spectrum of Compound **32** (376 MHz, $CDCl_3$)



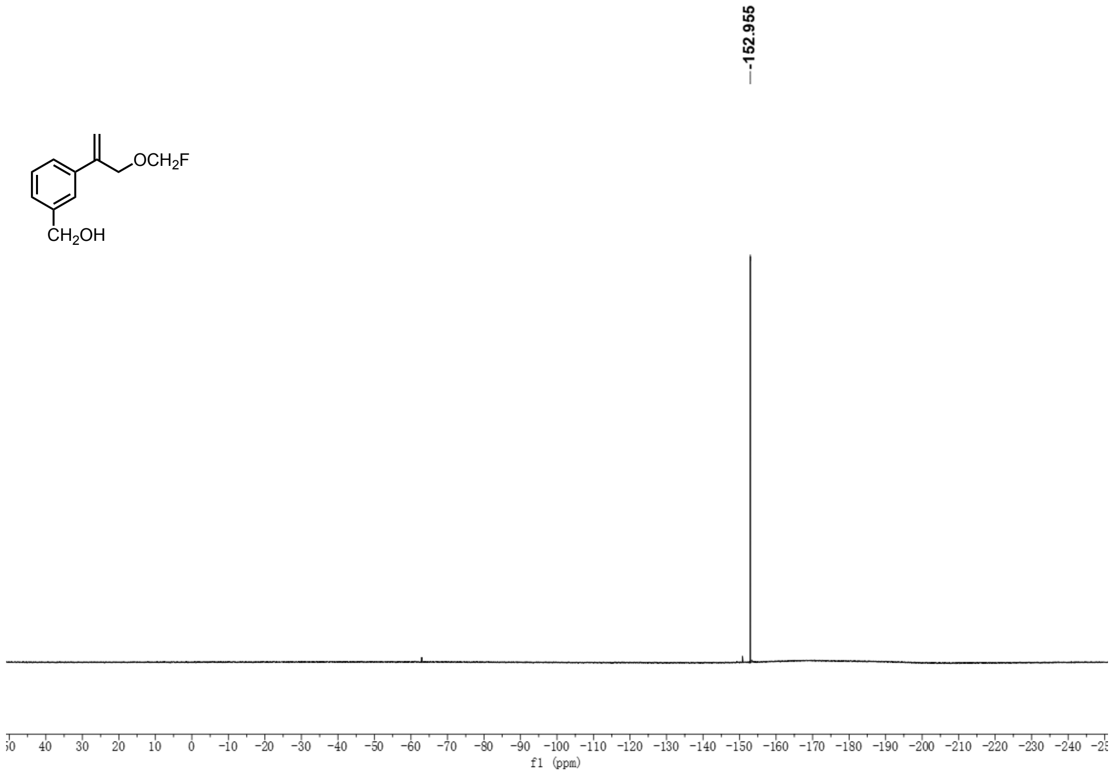
^{1}H NMR Spectrum of Compound **33** (400 MHz, $CDCl_3$)



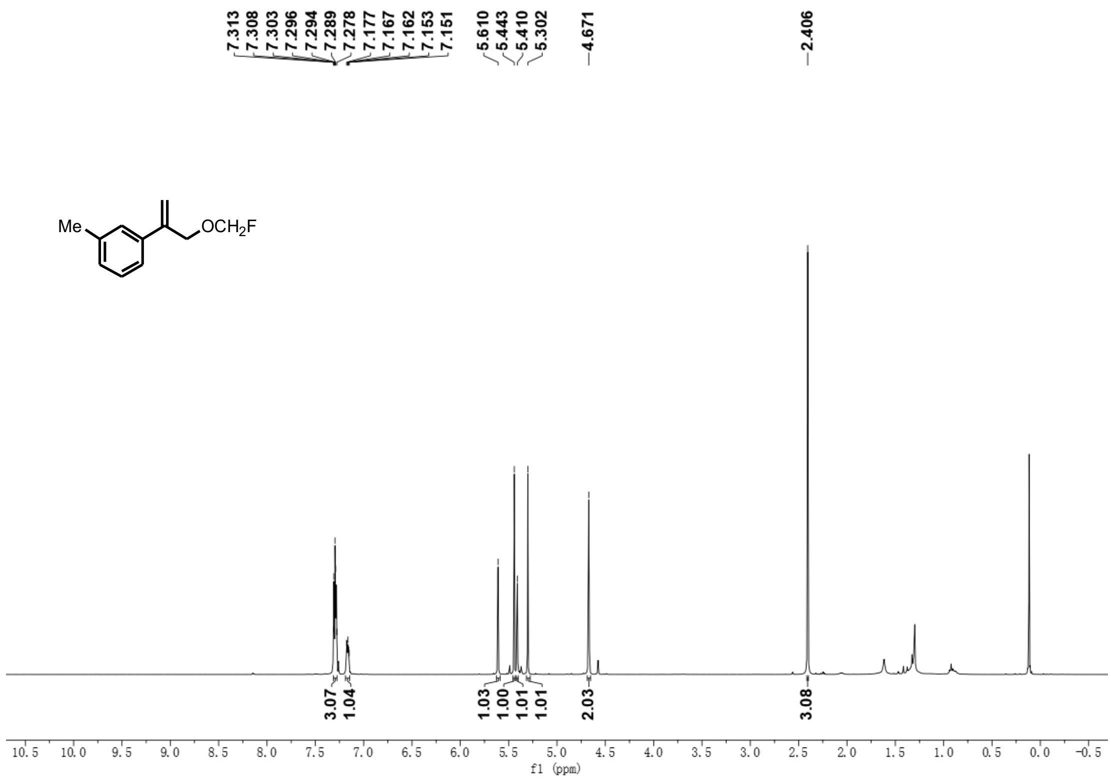
^{13}C NMR Spectrum of Compound **33** (151 MHz, $CDCl_3$)



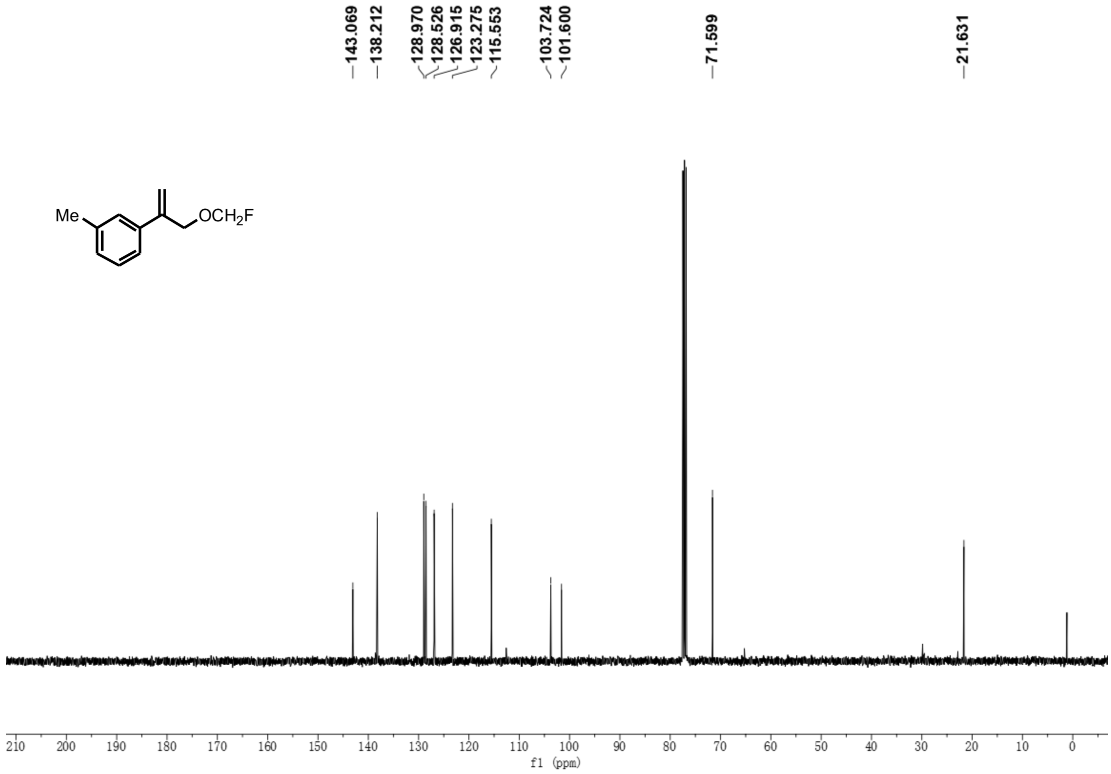
^{19}F NMR Spectrum of Compound **33** (376 MHz, $CDCl_3$)



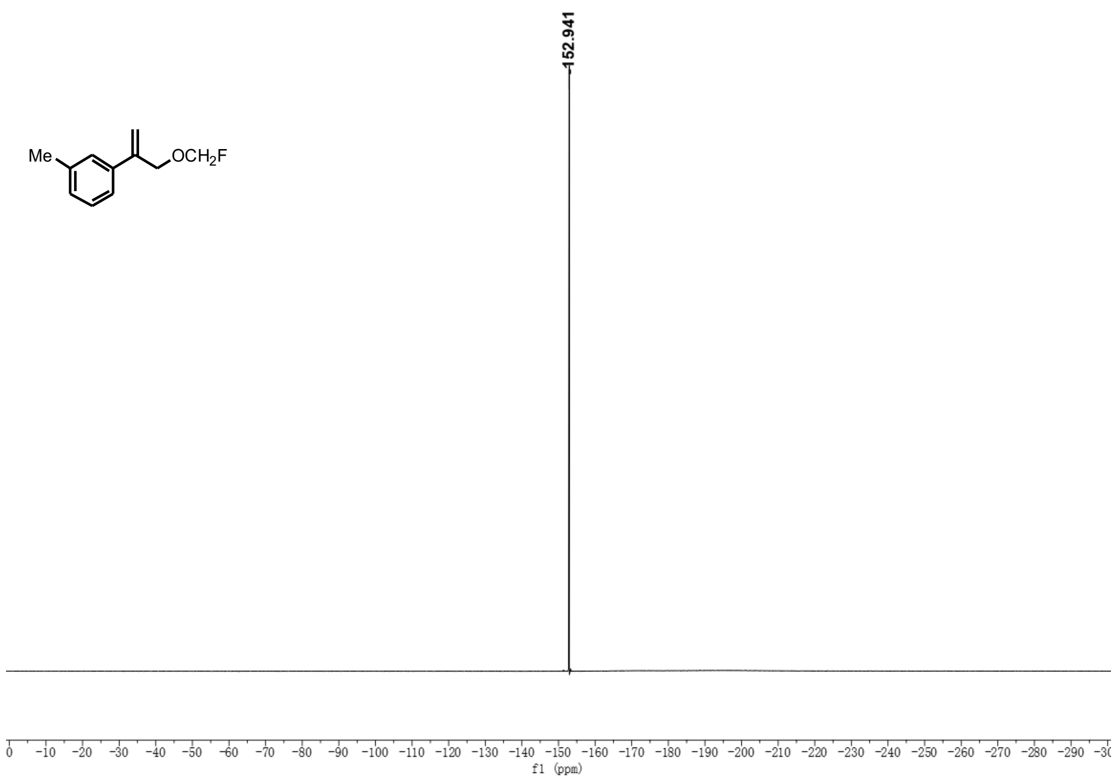
^{1}H NMR Spectrum of Compound **34** (400 MHz, $CDCl_3$)



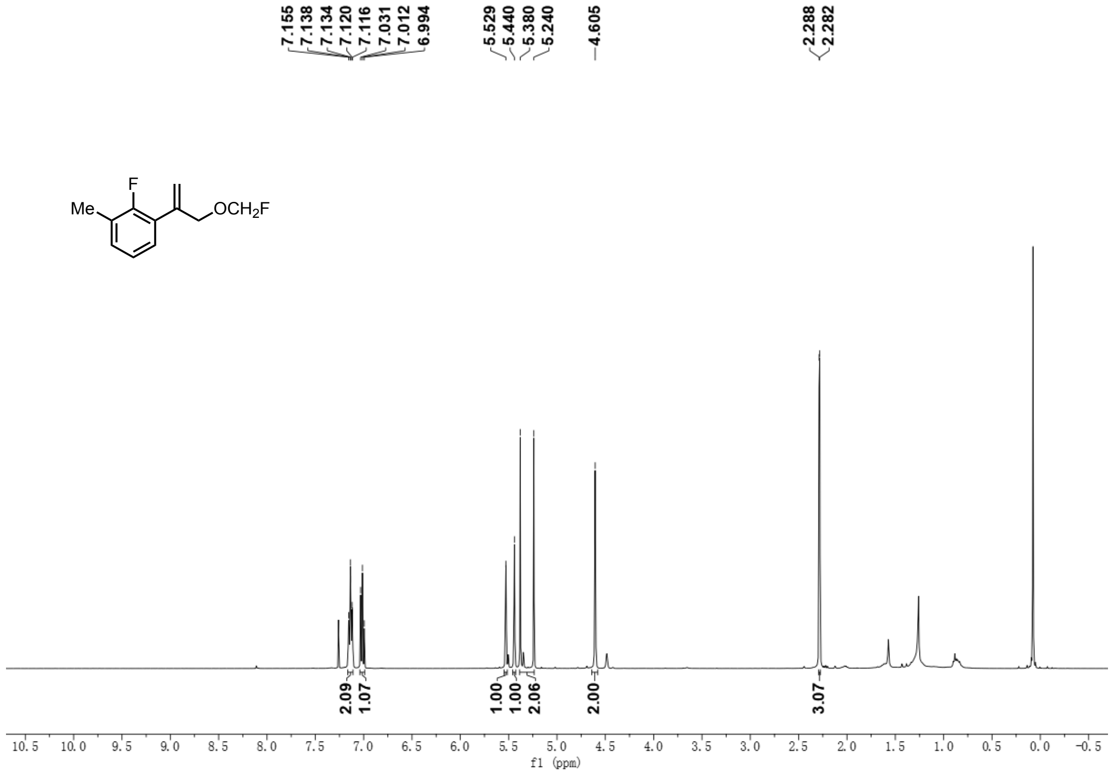
^{13}C NMR Spectrum of Compound **34** (101 MHz, $CDCl_3$)



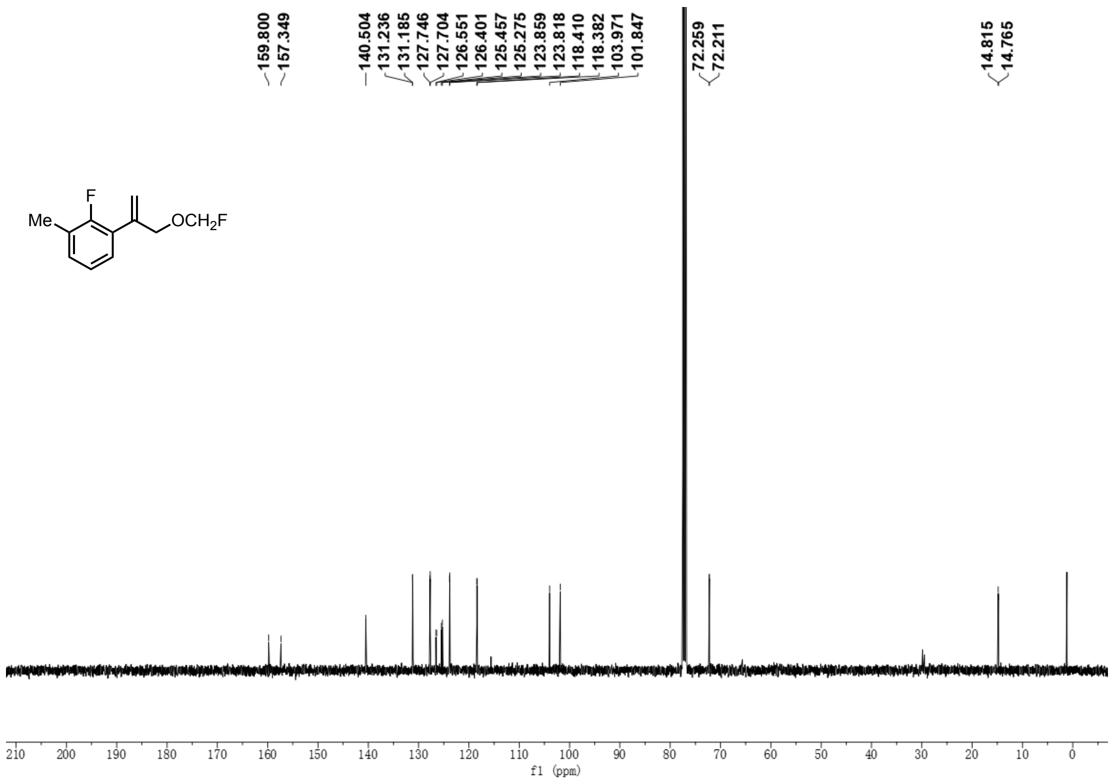
^{19}F NMR Spectrum of Compound **34** (376 MHz, $CDCl_3$)



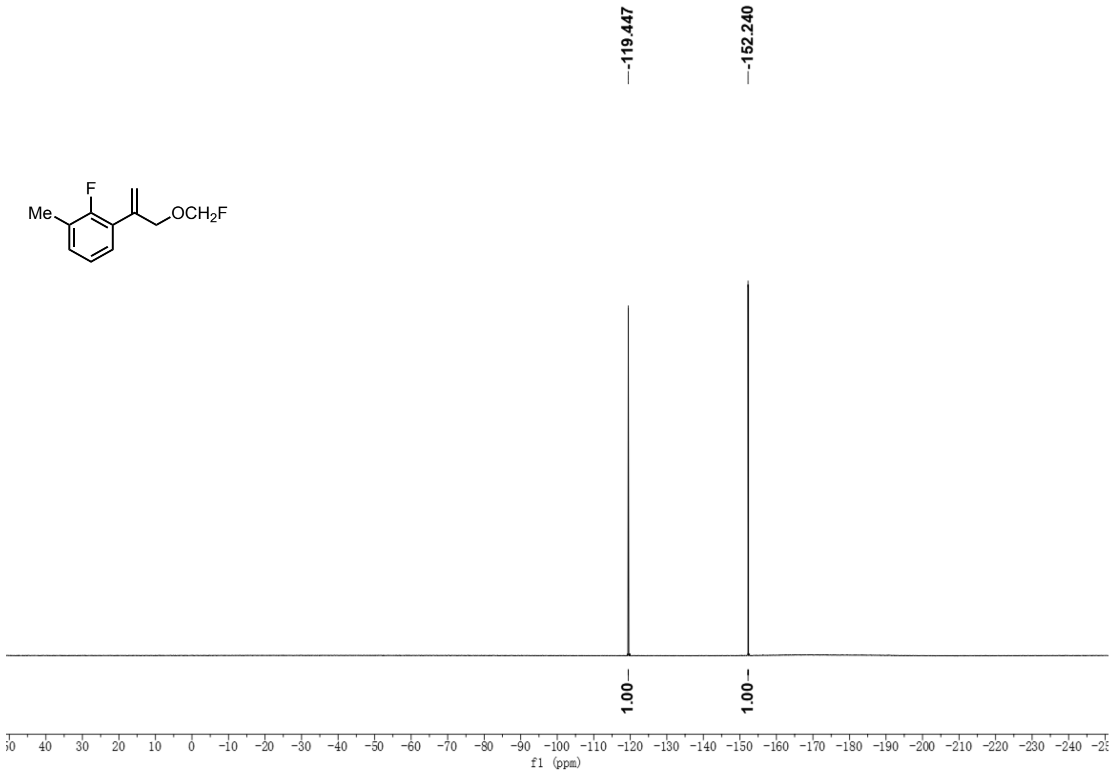
[1]H NMR Spectrum of Compound **35** (400 MHz, $CDCl_3$)



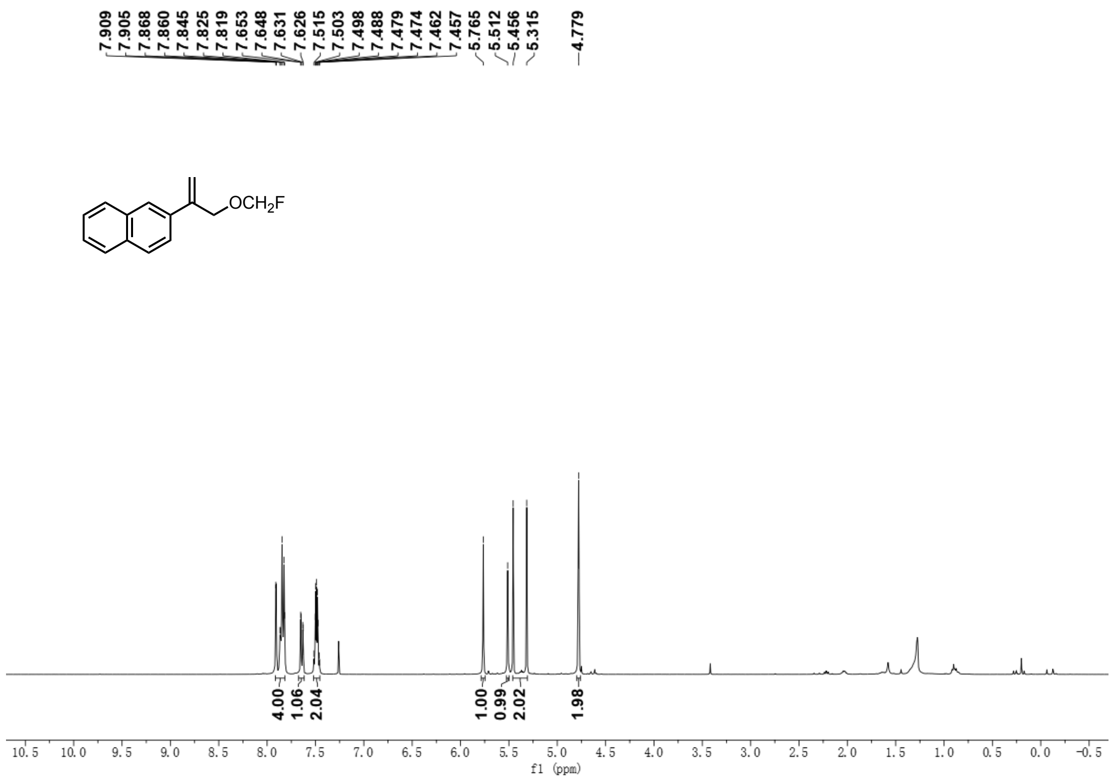
[13]C NMR Spectrum of Compound **35** (101 MHz, $CDCl_3$)



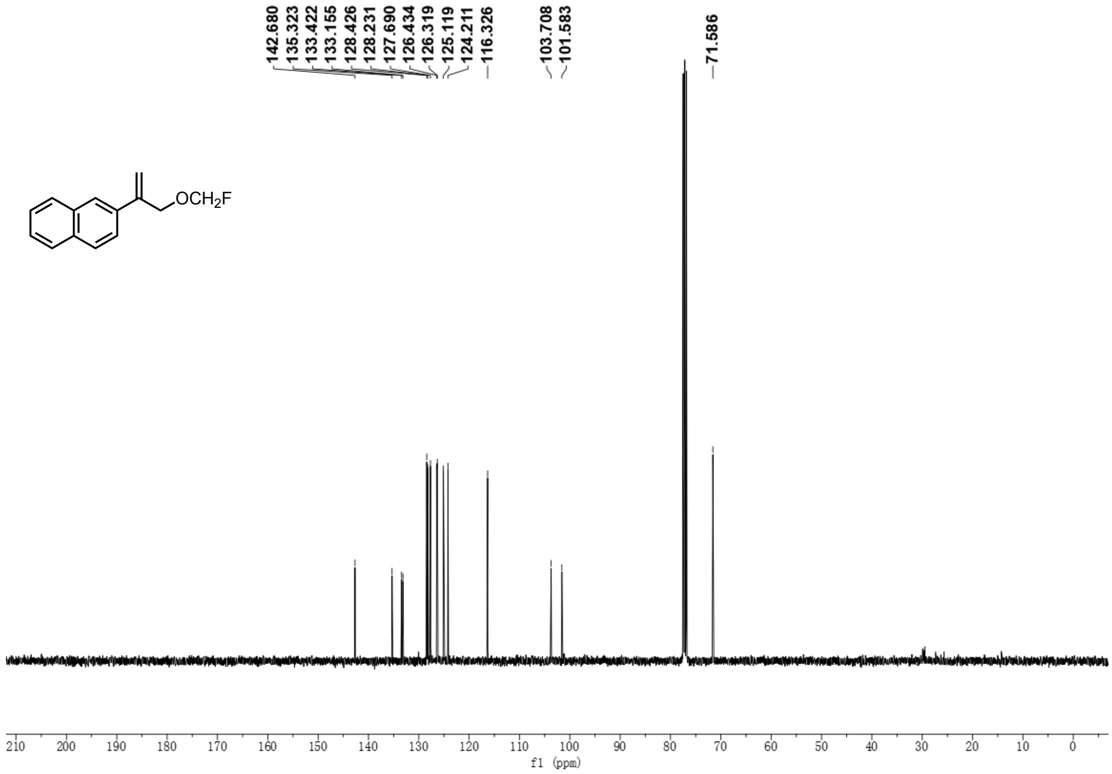
^{19}F NMR Spectrum of Compound **35** (376 MHz, $CDCl_3$)



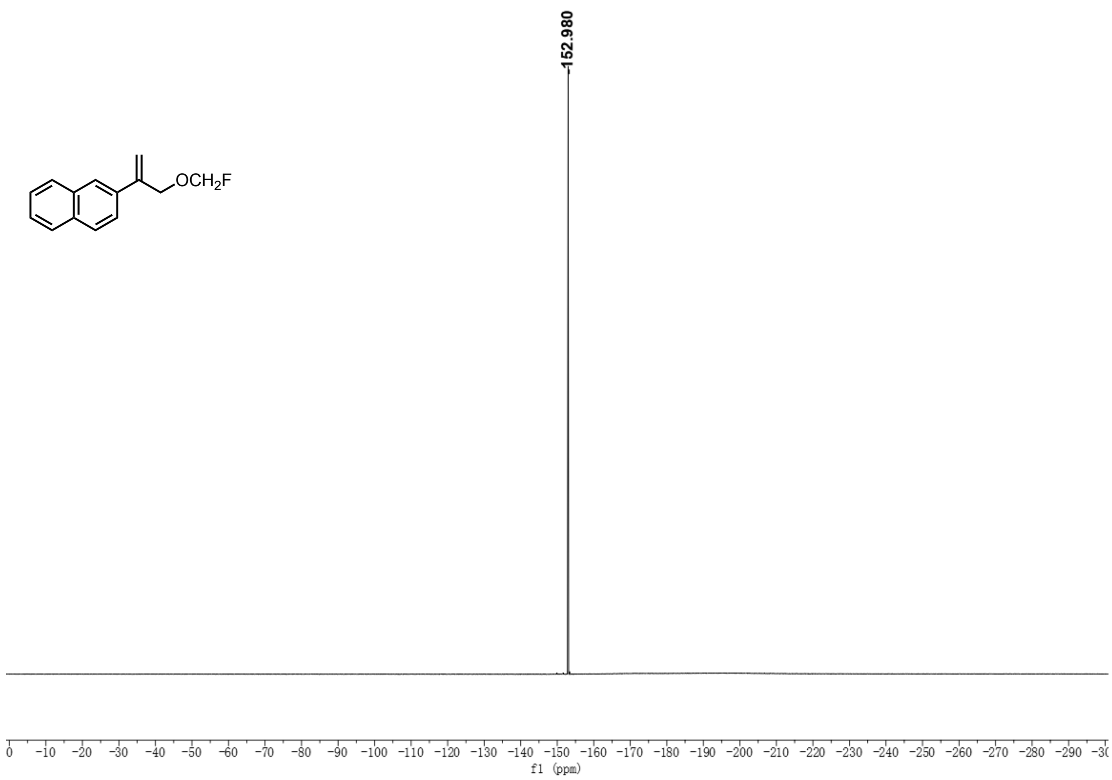
^{1}H NMR Spectrum of Compound **36** (400 MHz, $CDCl_3$)



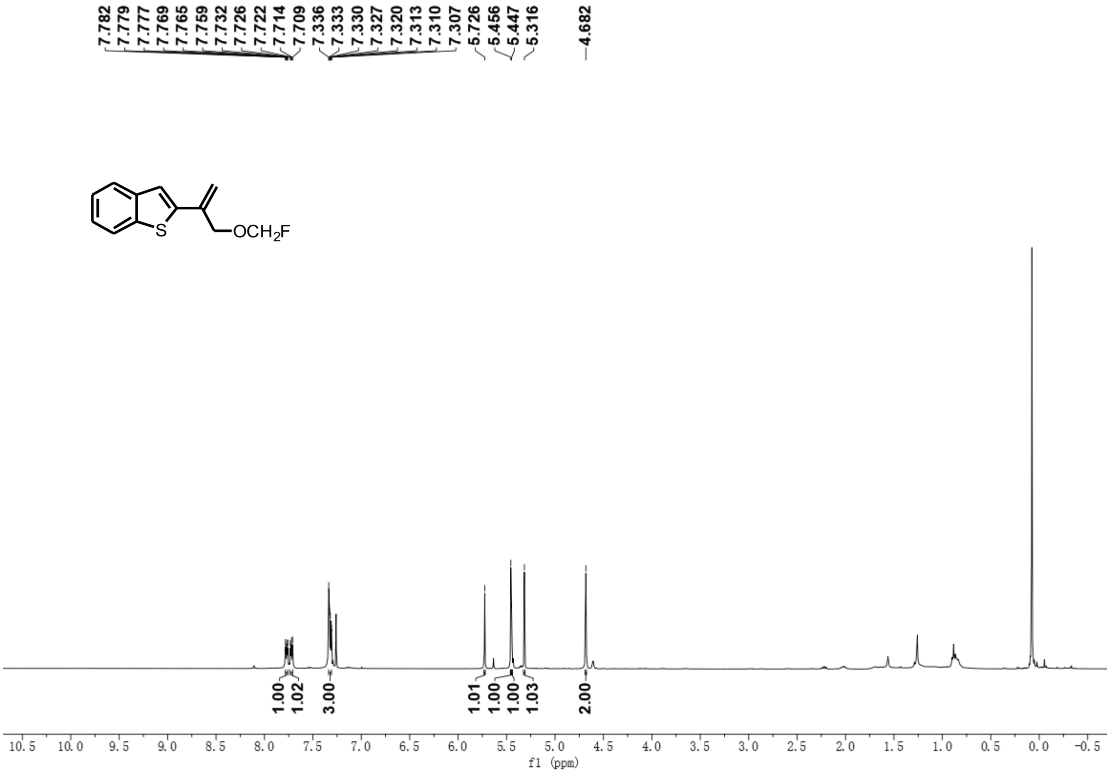
^{13}C NMR Spectrum of Compound **36** (101 MHz, $CDCl_3$)



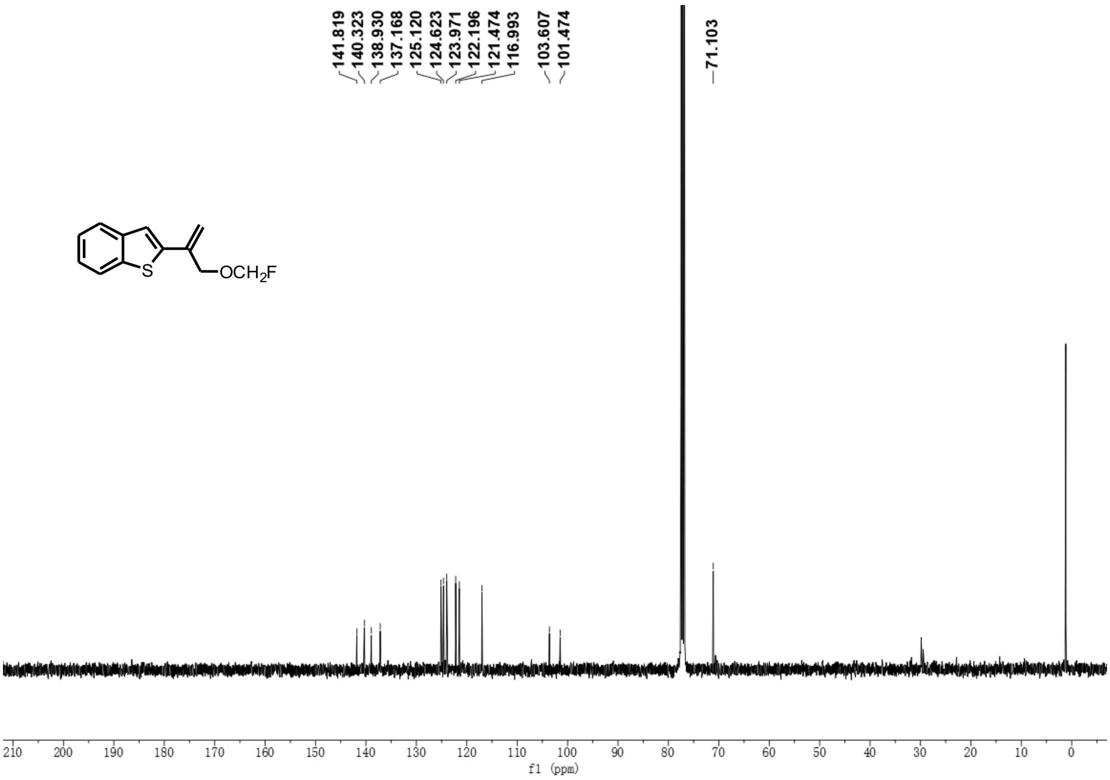
^{19}F NMR Spectrum of Compound **36** (376 MHz, $CDCl_3$)



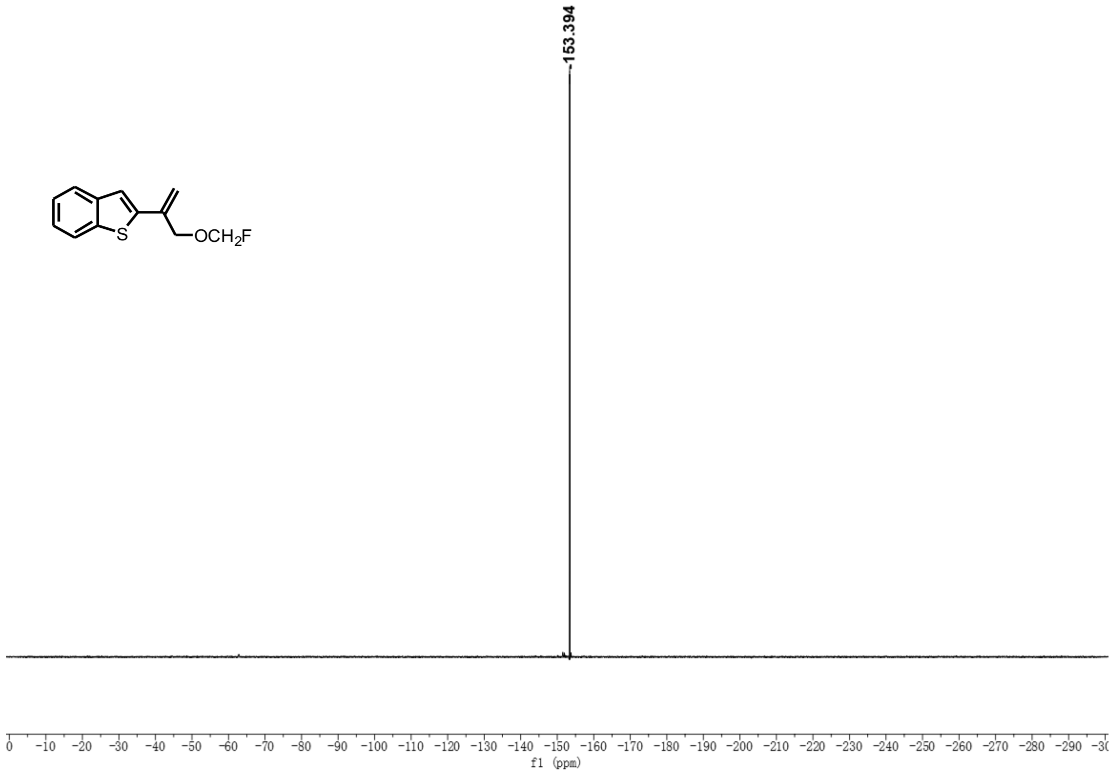
[1]H NMR Spectrum of Compound **37** (400 MHz, $CDCl_3$)



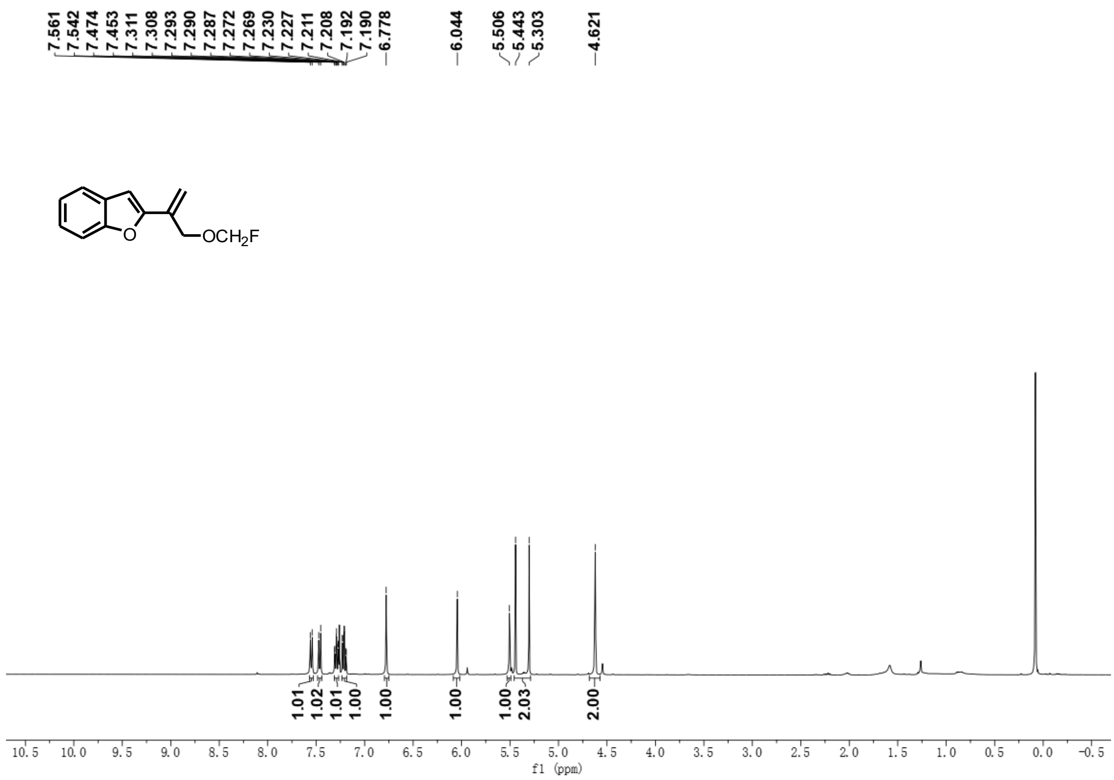
[13]C NMR Spectrum of Compound **37** (101 MHz, $CDCl_3$)



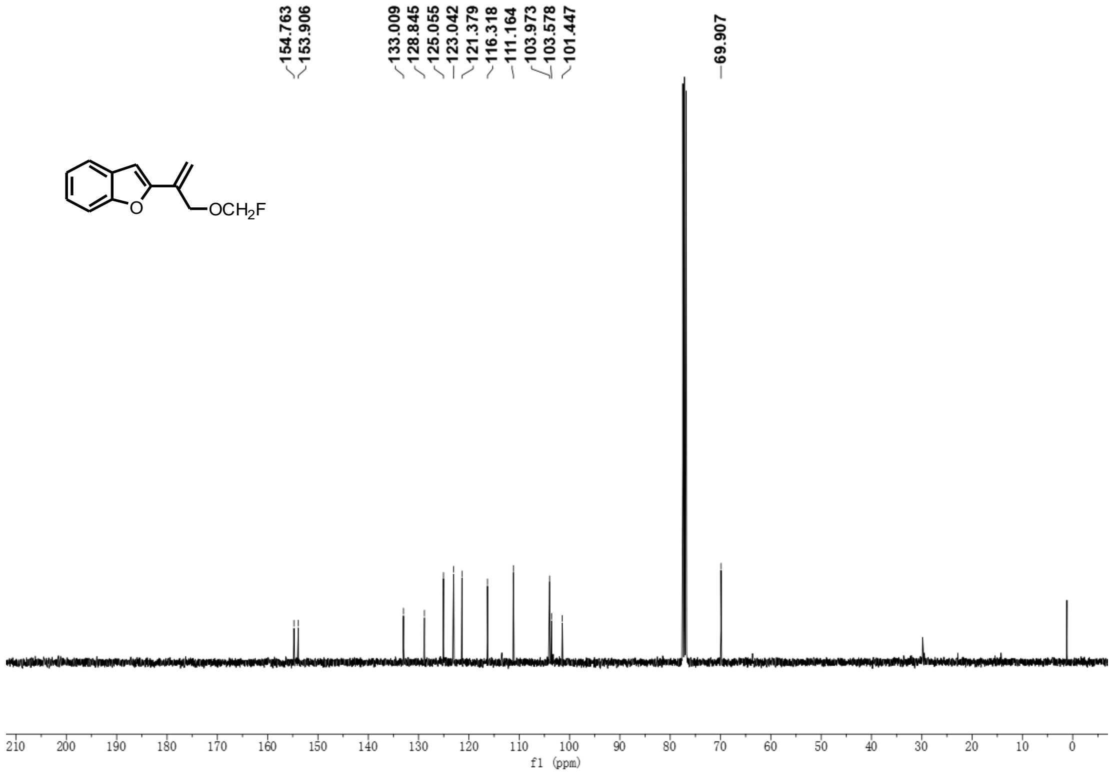
^{19}F NMR Spectrum of Compound **37** (376 MHz, $CDCl_3$)



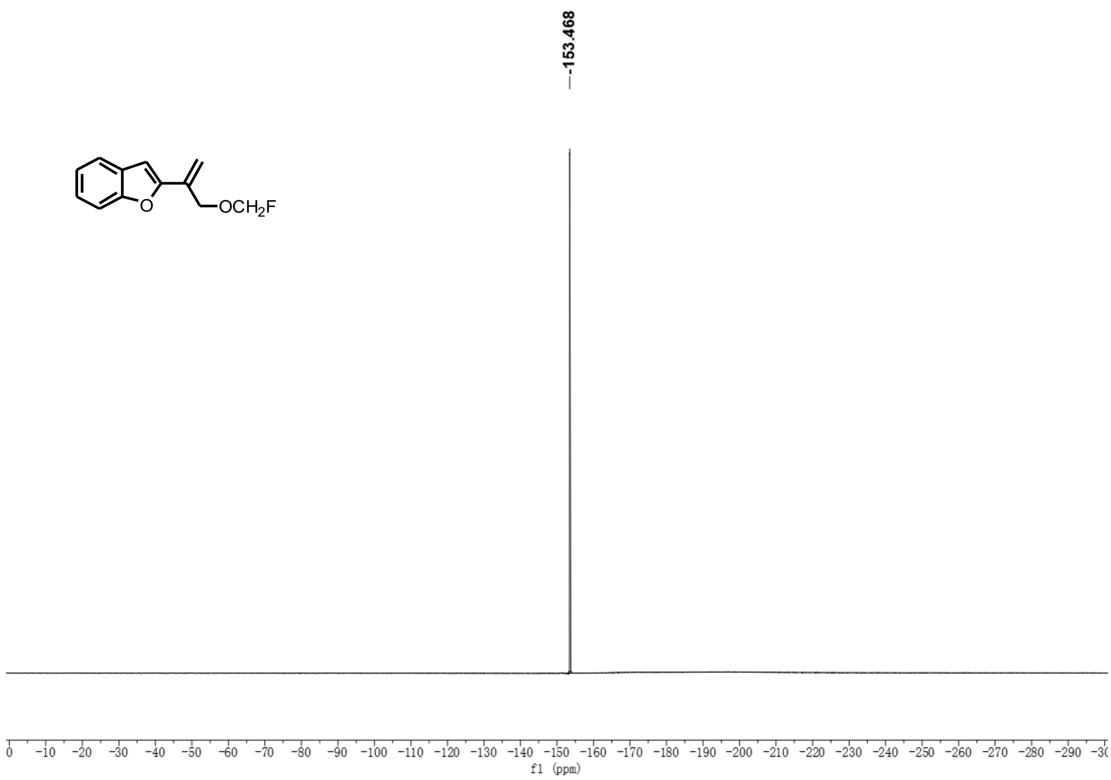
^{1}H NMR Spectrum of Compound **38** (400 MHz, $CDCl_3$)



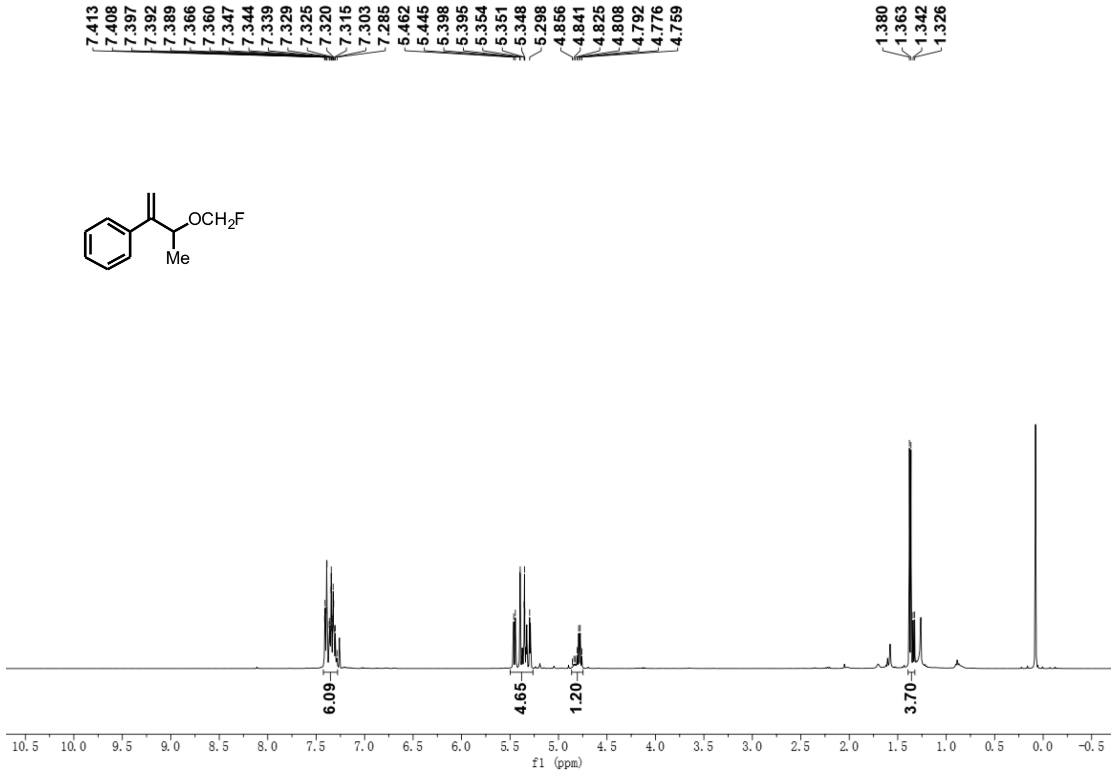
^{13}C NMR Spectrum of Compound **38** (101 MHz, $CDCl_3$)



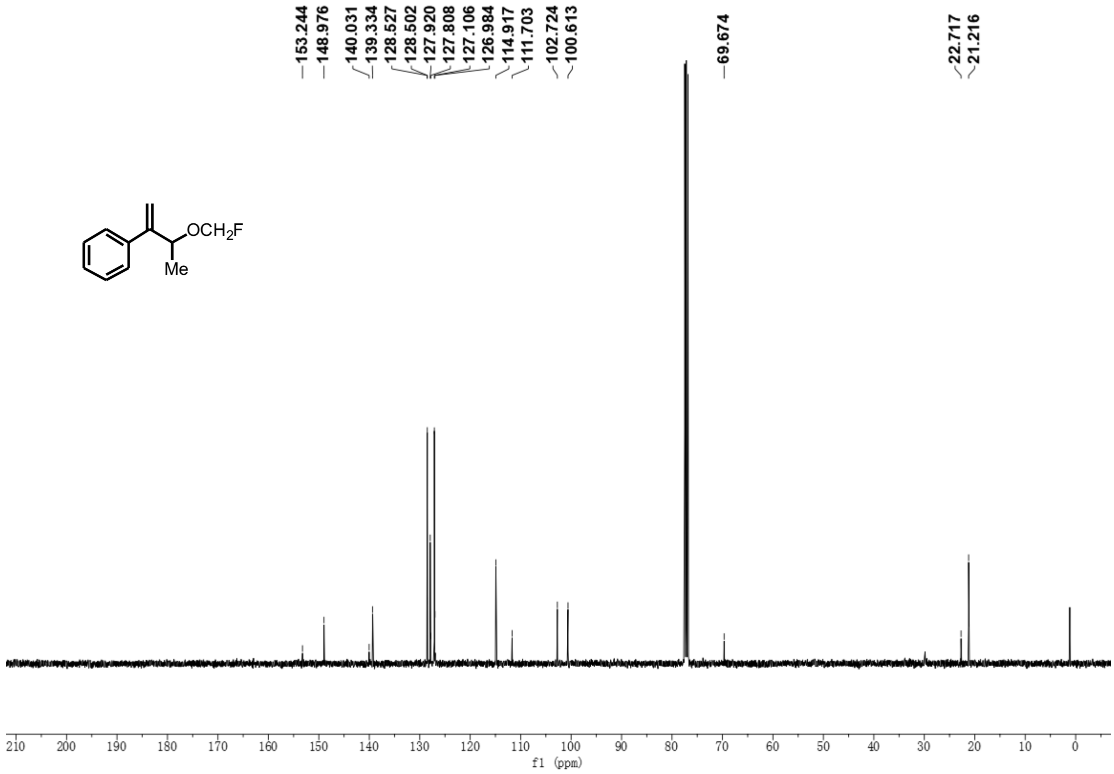
^{19}F NMR Spectrum of Compound **38** (376 MHz, $CDCl_3$)



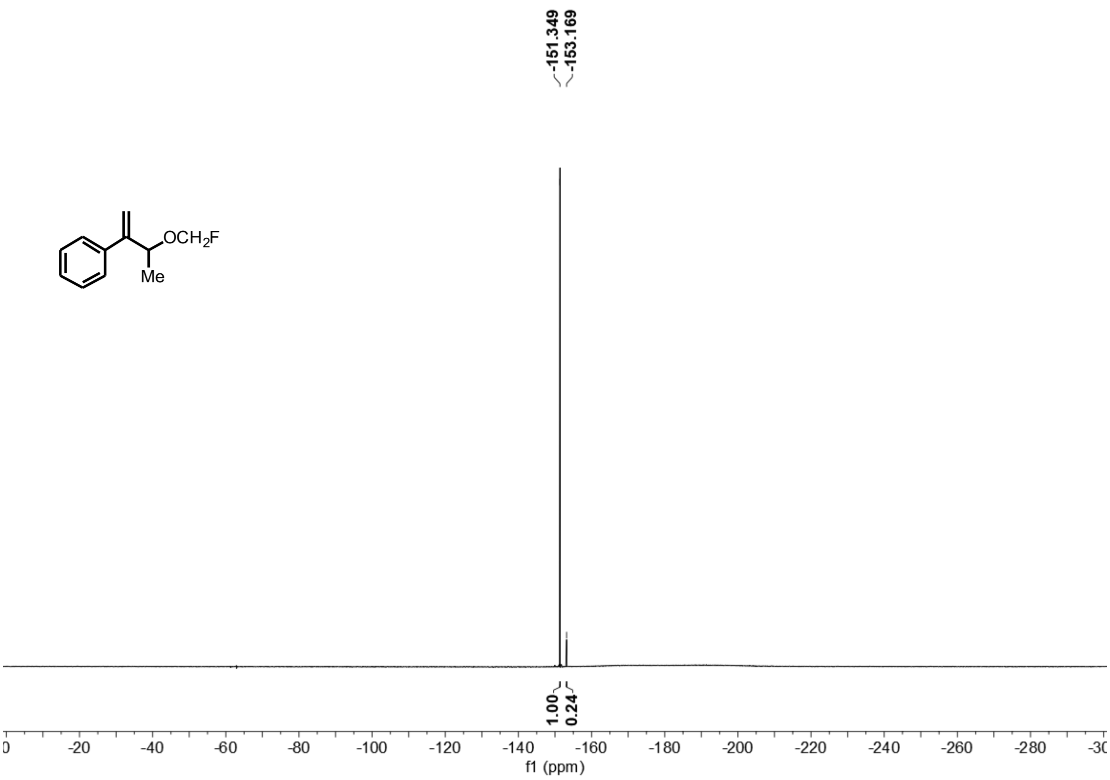
[1]H NMR Spectrum of Compound **39** (400 MHz, $CDCl_3$)



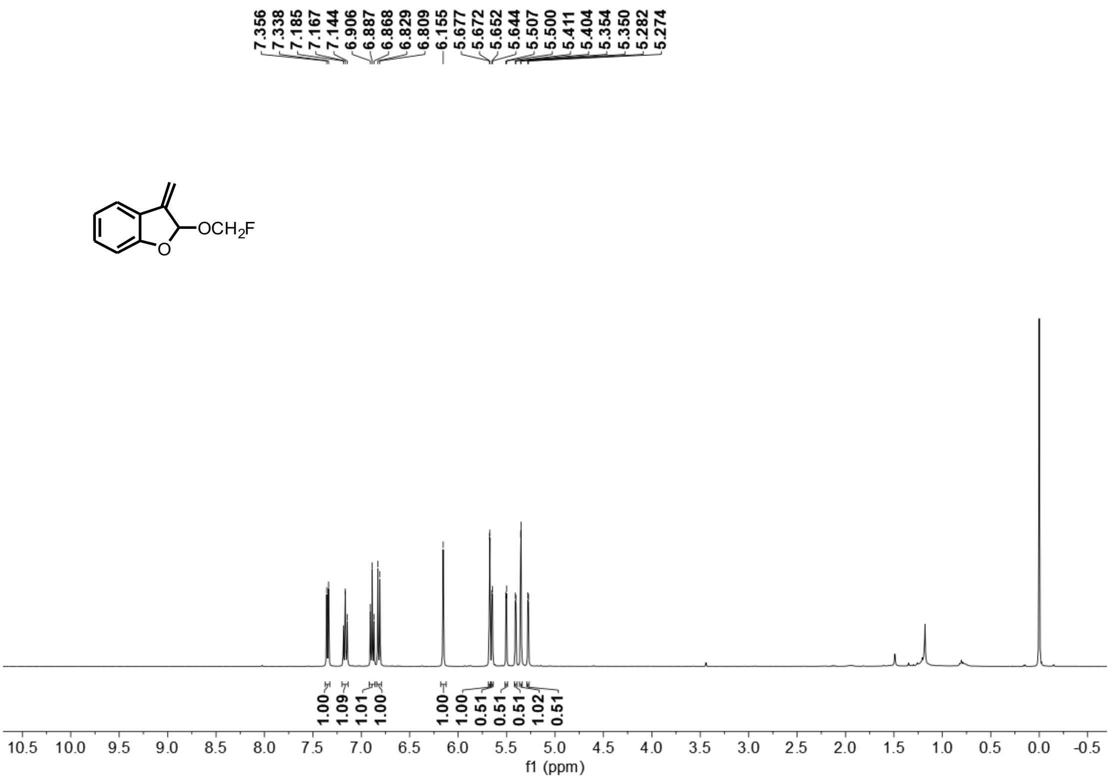
[13]C NMR Spectrum of Compound **39** (101 MHz, $CDCl_3$)



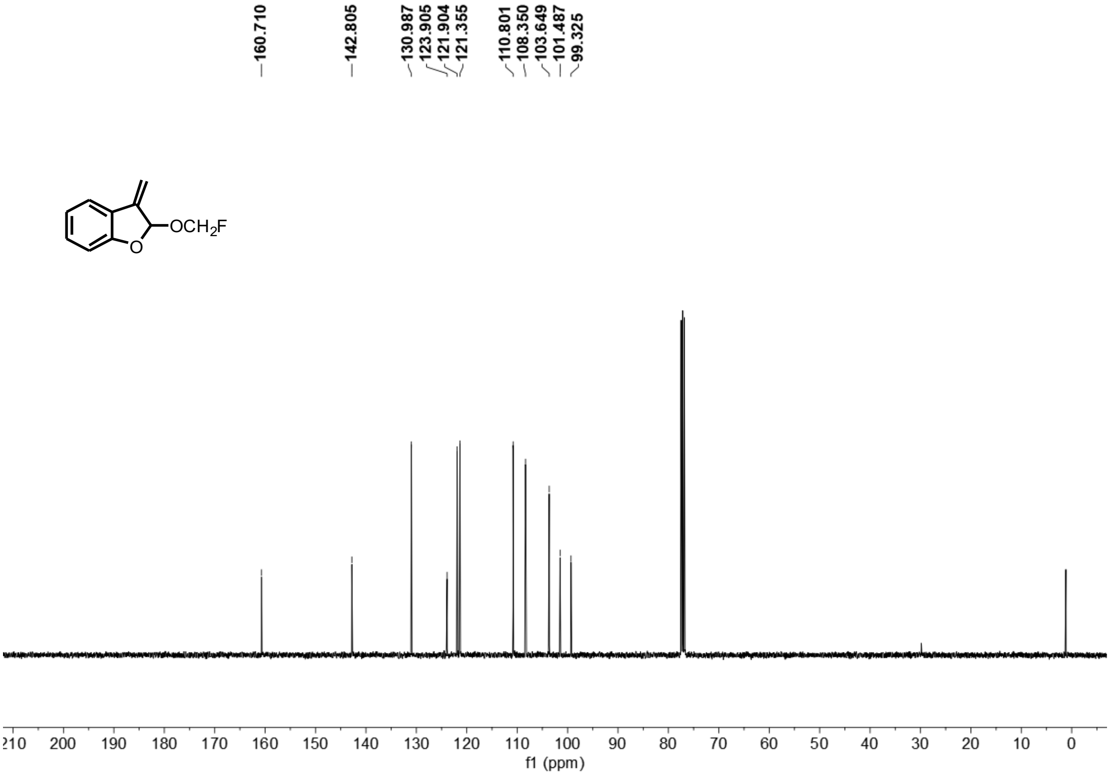
^{19}F NMR Spectrum of Compound **39** (376 MHz, $CDCl_3$)



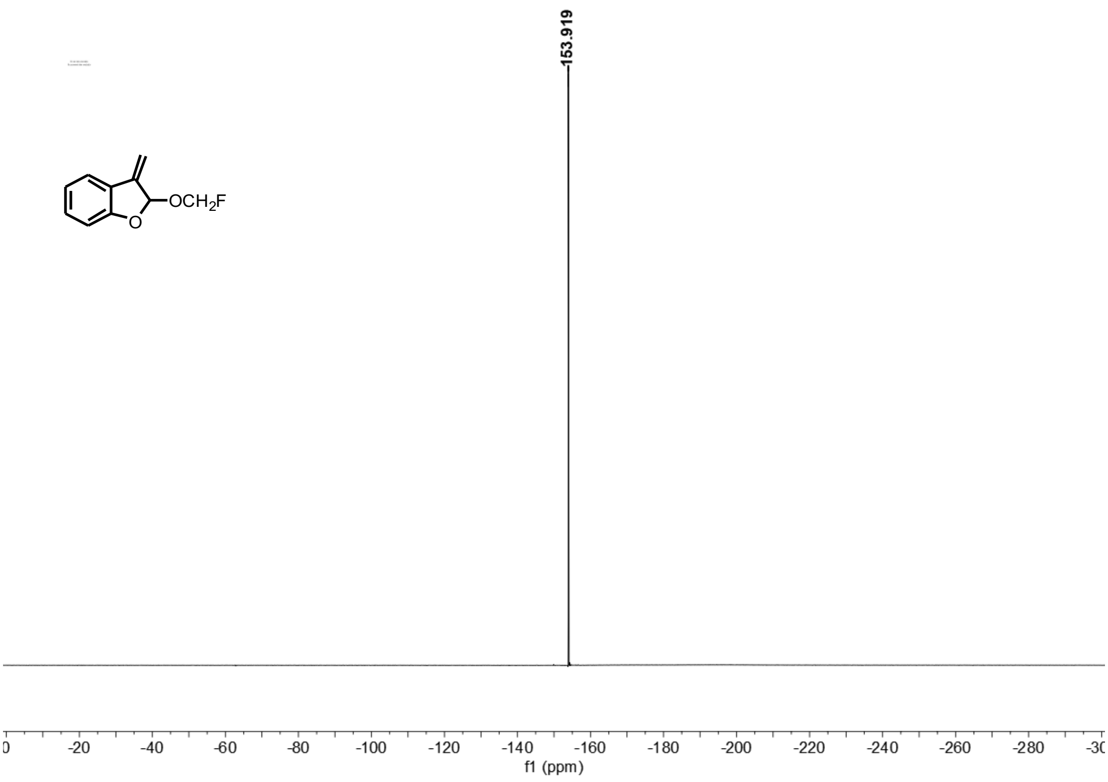
^{1}H NMR Spectrum of Compound **40** (400 MHz, $CDCl_3$)



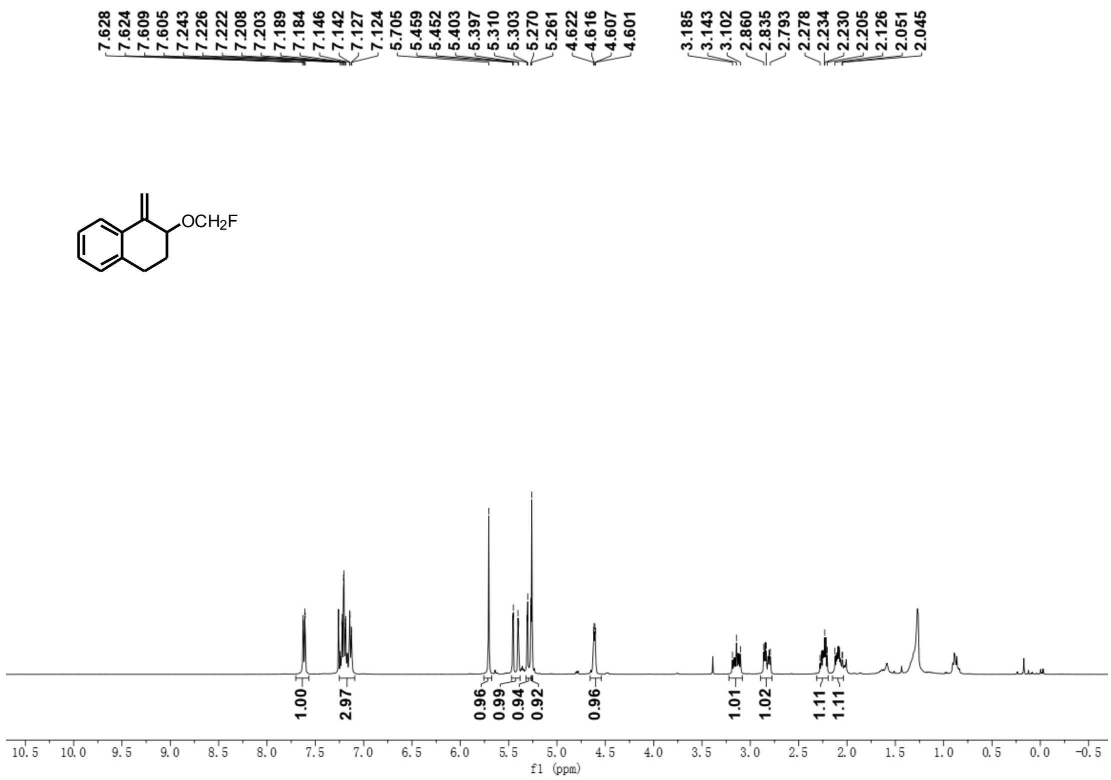
^{13}C NMR Spectrum of Compound **40** (101 MHz, $CDCl_3$)



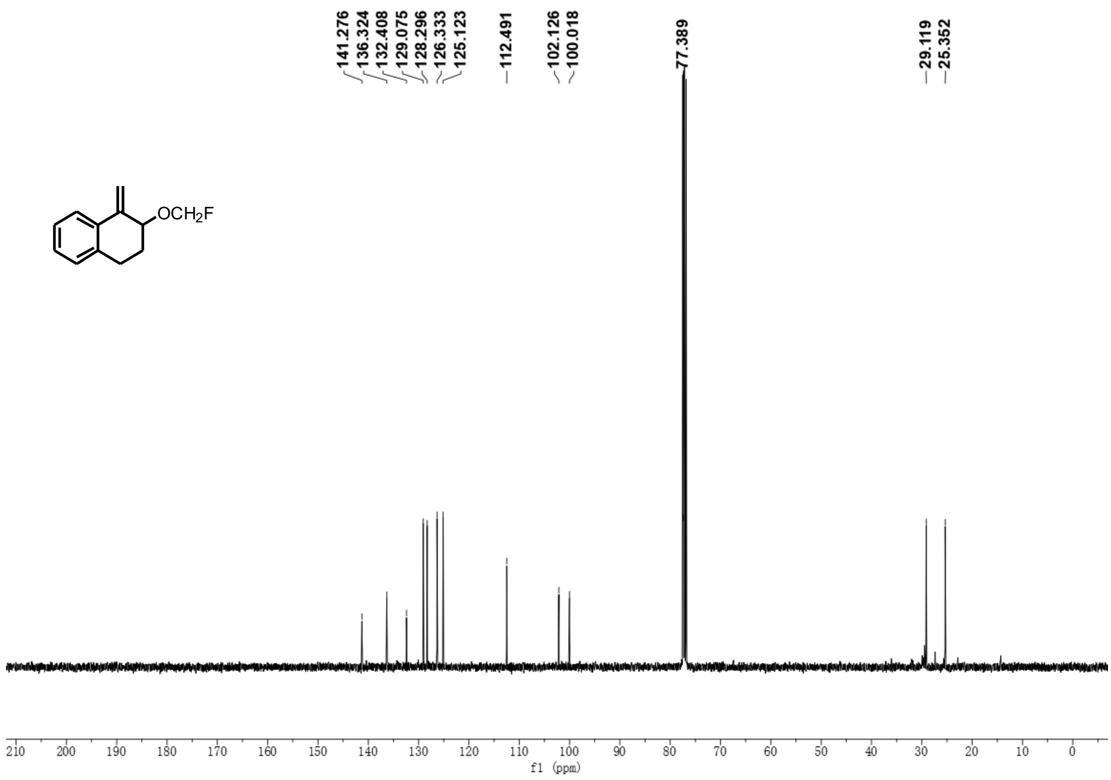
^{19}F NMR Spectrum of Compound **40** (376 MHz, $CDCl_3$)



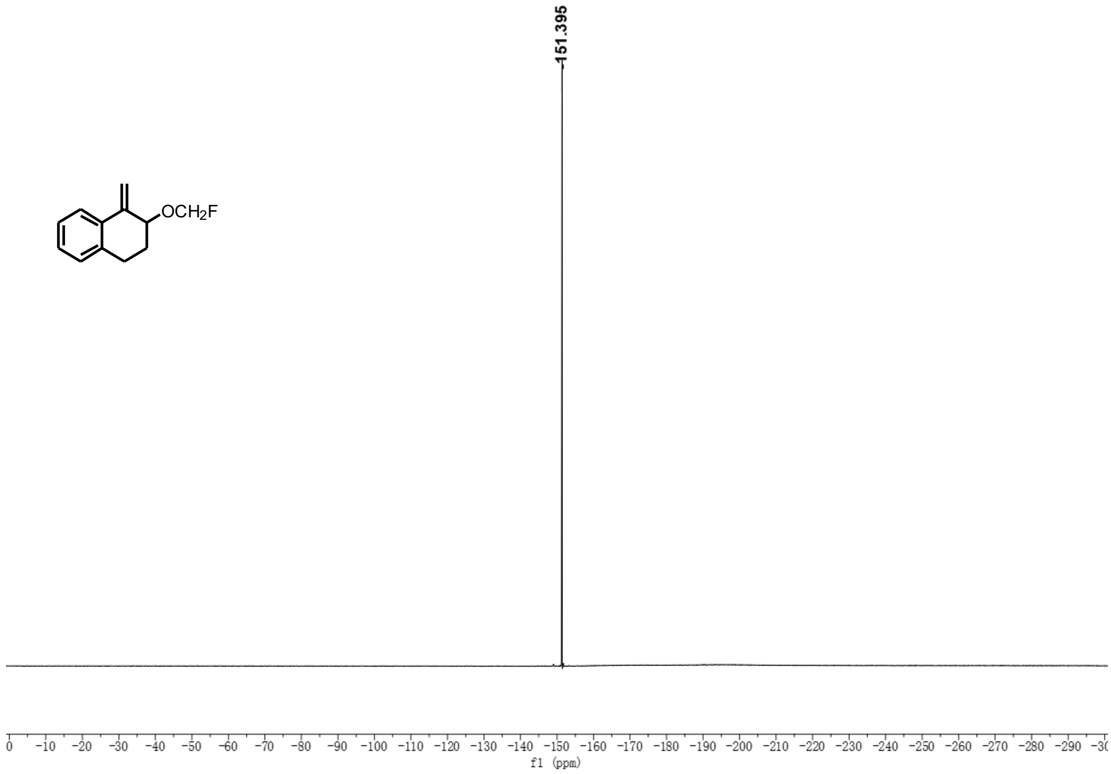
[1]H NMR Spectrum of Compound **41** (400 MHz, $CDCl_3$)



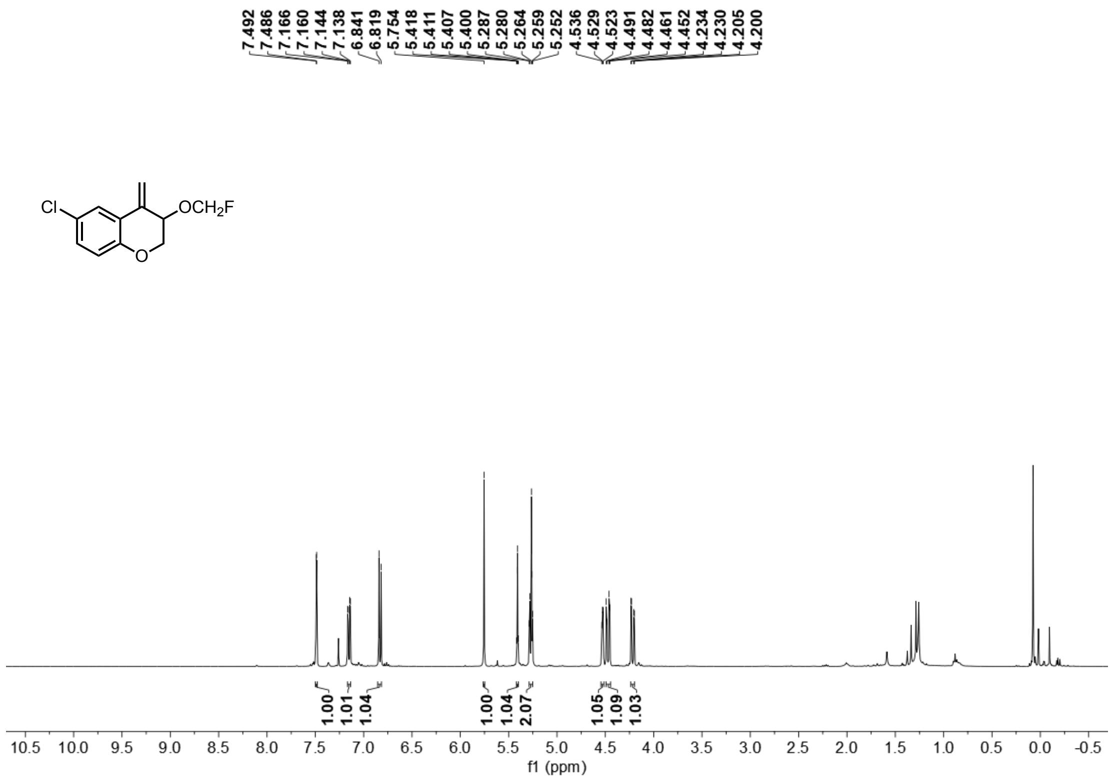
[13]C NMR Spectrum of Compound **41** (101 MHz, $CDCl_3$)



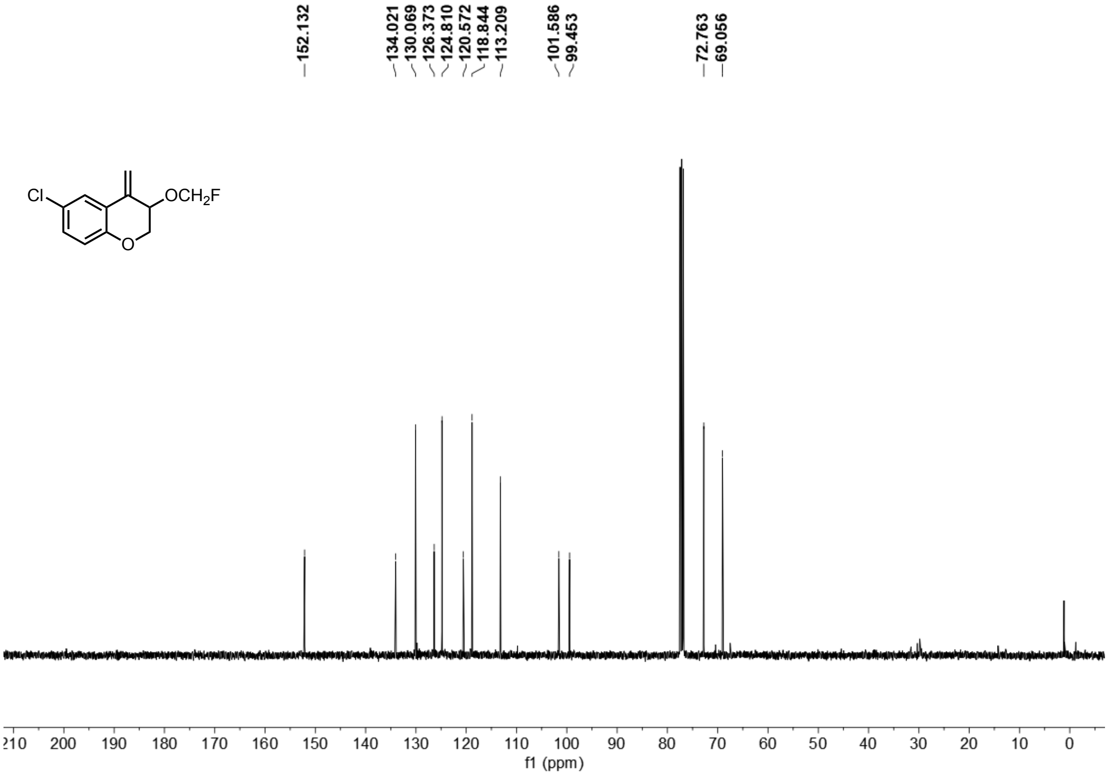
^{19}F NMR Spectrum of Compound **41** (376 MHz, $CDCl_3$)



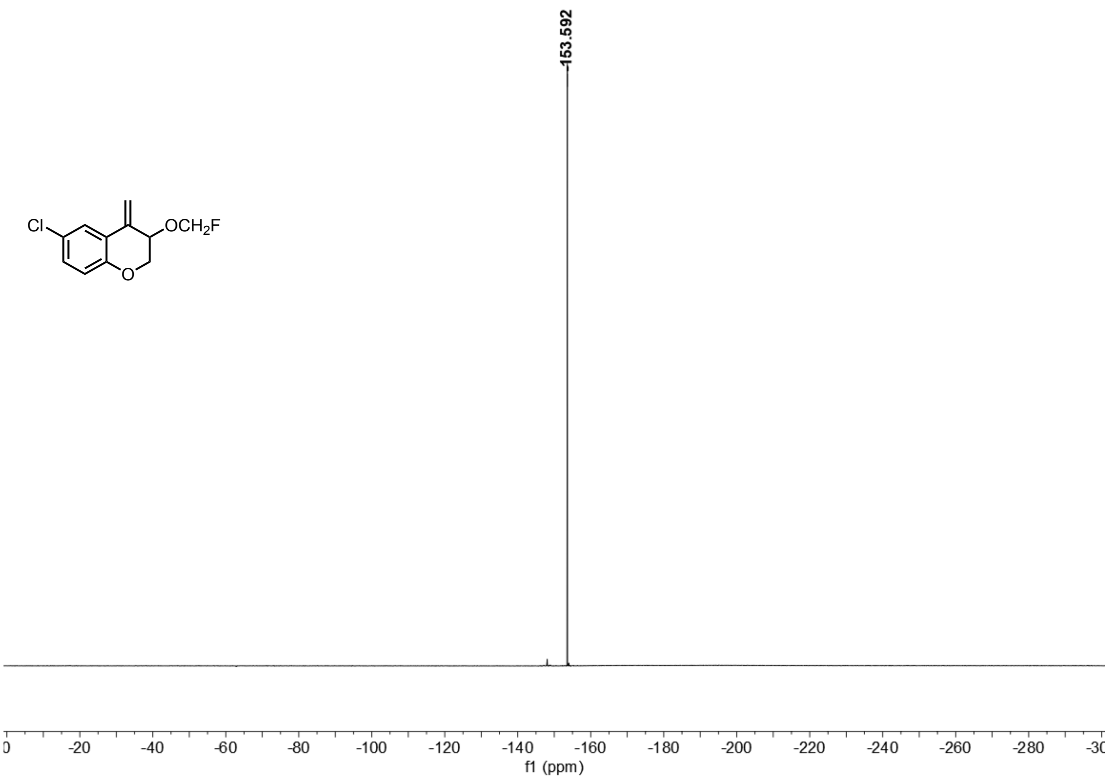
^{1}H NMR Spectrum of Compound **42** (400 MHz, $CDCl_3$)



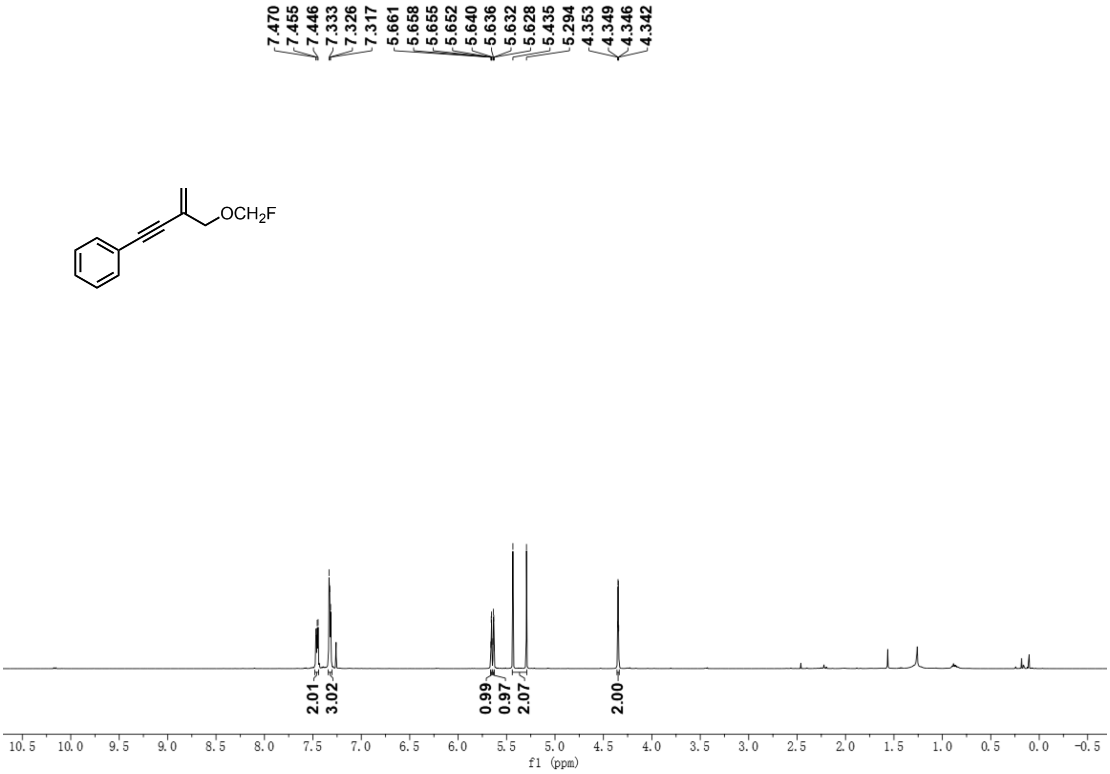
^{13}C NMR Spectrum of Compound **42** (101 MHz, $CDCl_3$)



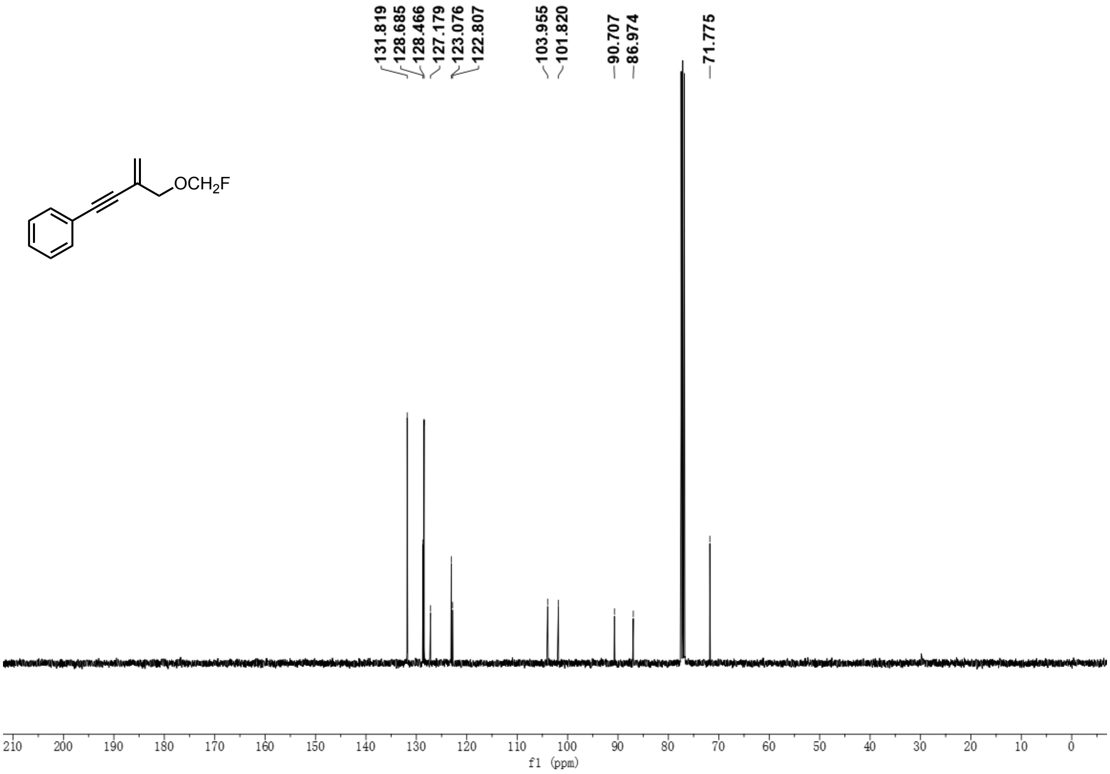
^{19}F NMR Spectrum of Compound **42** (376 MHz, $CDCl_3$)



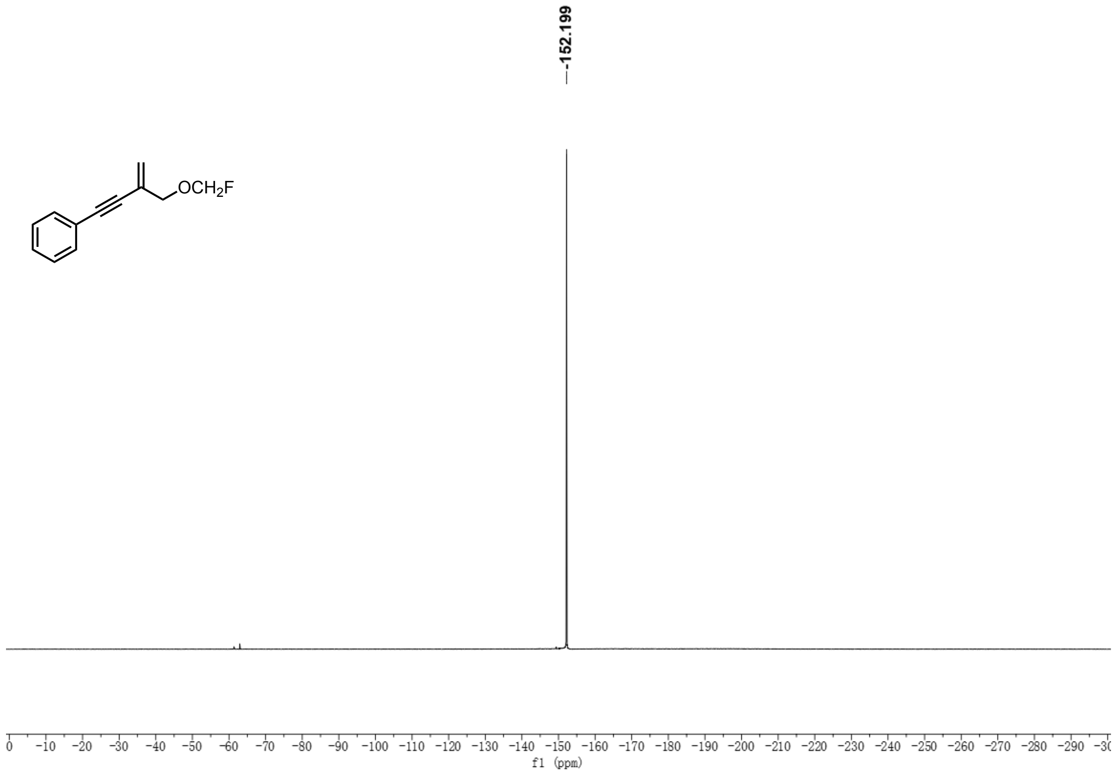
^{1}H NMR Spectrum of Compound **43** (400 MHz, $CDCl_3$)



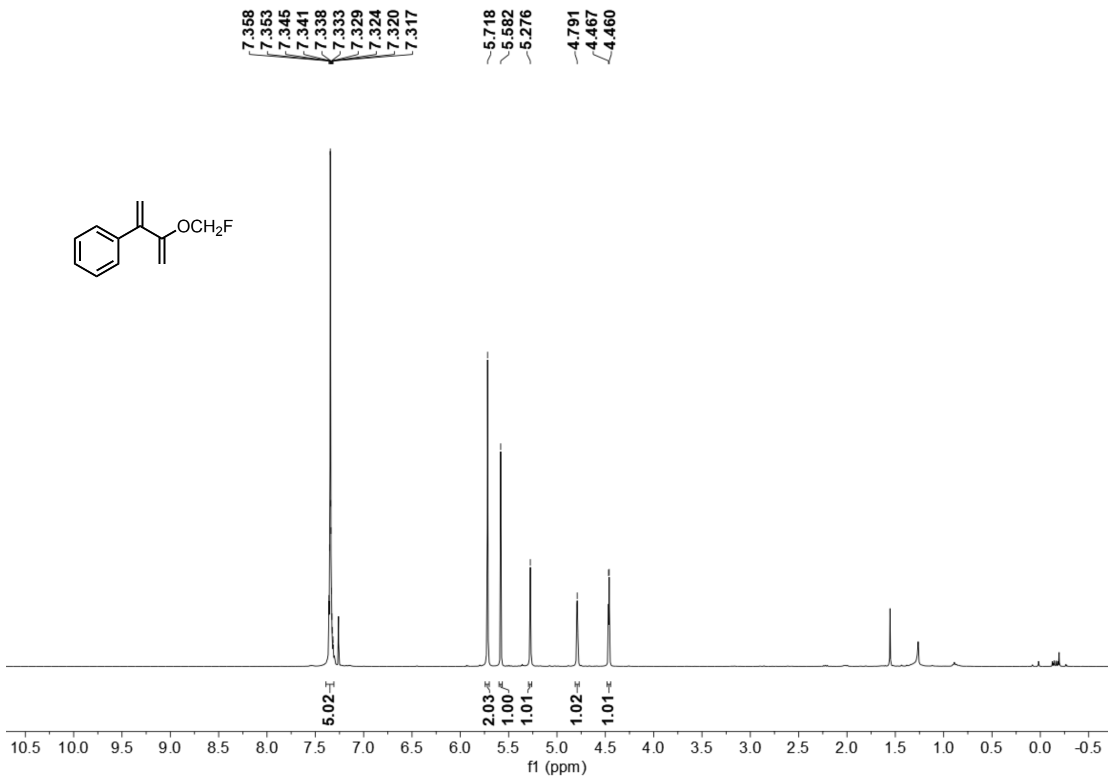
^{13}C NMR Spectrum of Compound **43** (101 MHz, $CDCl_3$)



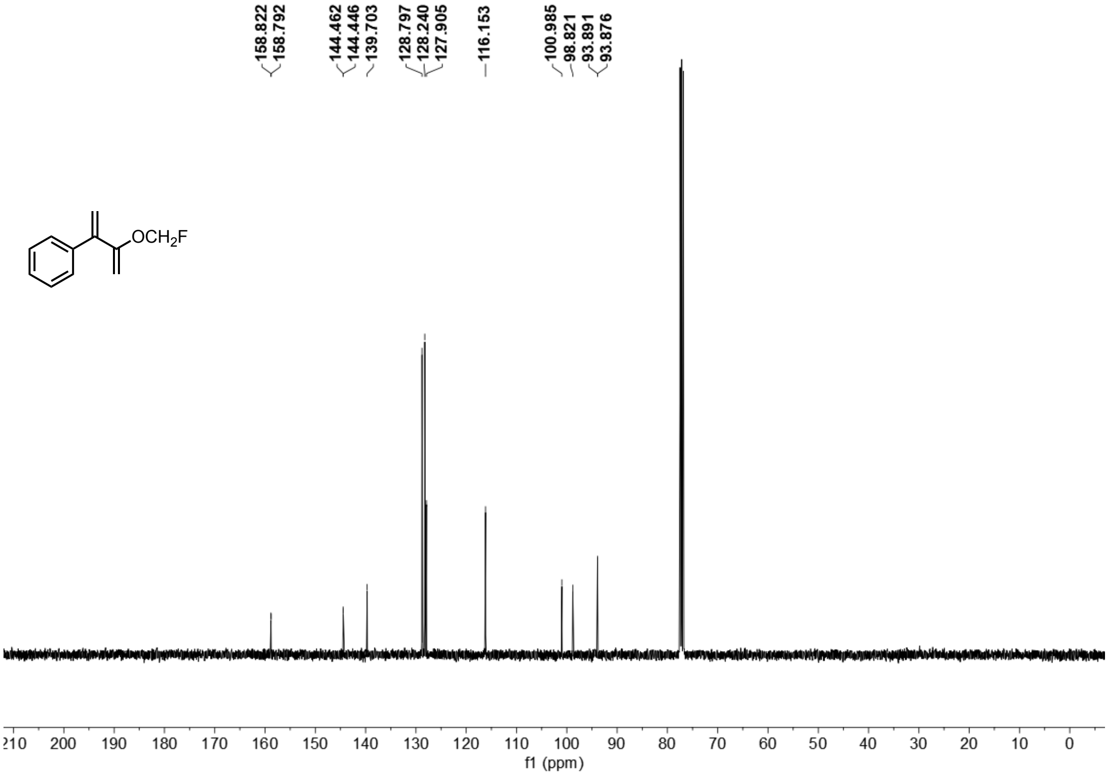
^{19}F NMR Spectrum of Compound **43** (376 MHz, $CDCl_3$)



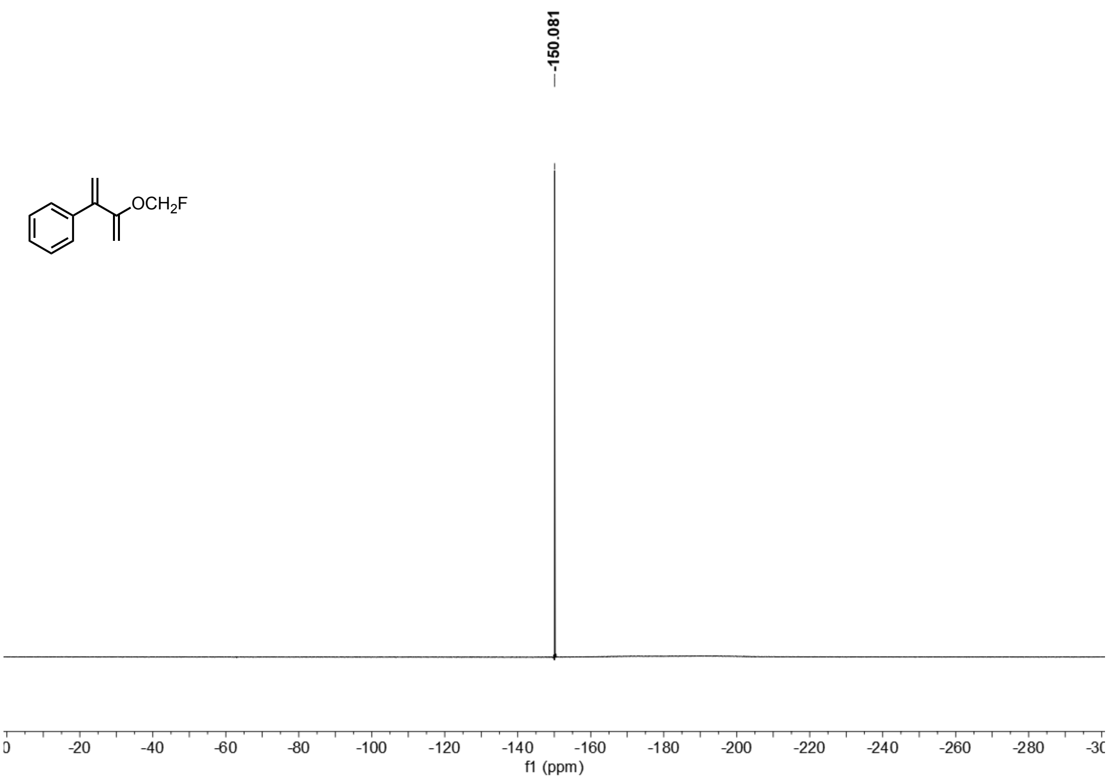
^{1}H NMR Spectrum of Compound **44** (400 MHz, $CDCl_3$)



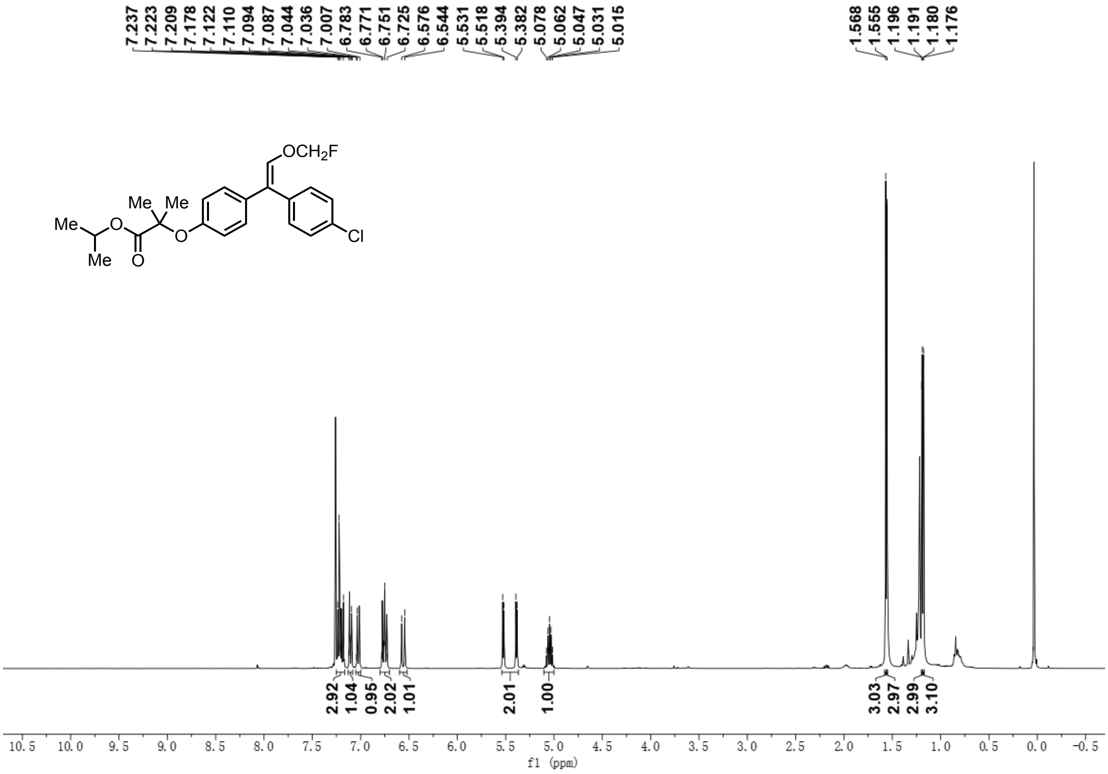
^{13}C NMR Spectrum of Compound **44** (101 MHz, $CDCl_3$)



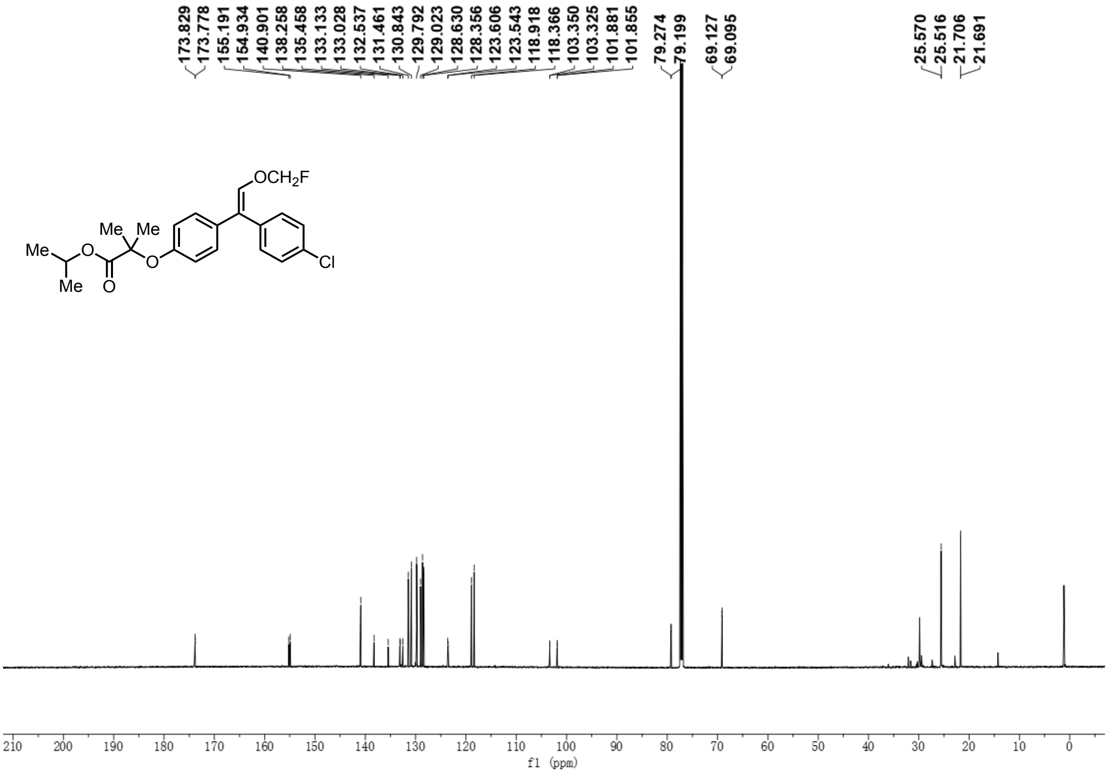
^{19}F NMR Spectrum of Compound **44** (376 MHz, $CDCl_3$)



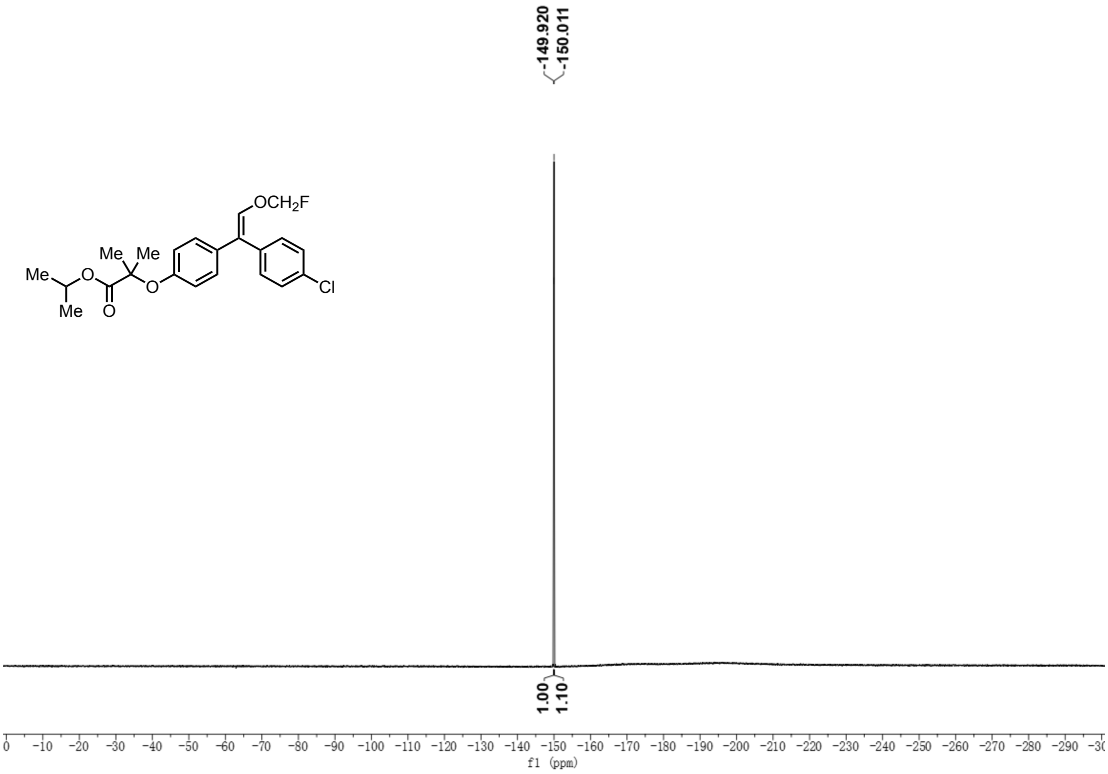
^{1}H NMR Spectrum of Compound **45** (400 MHz, $CDCl_3$)



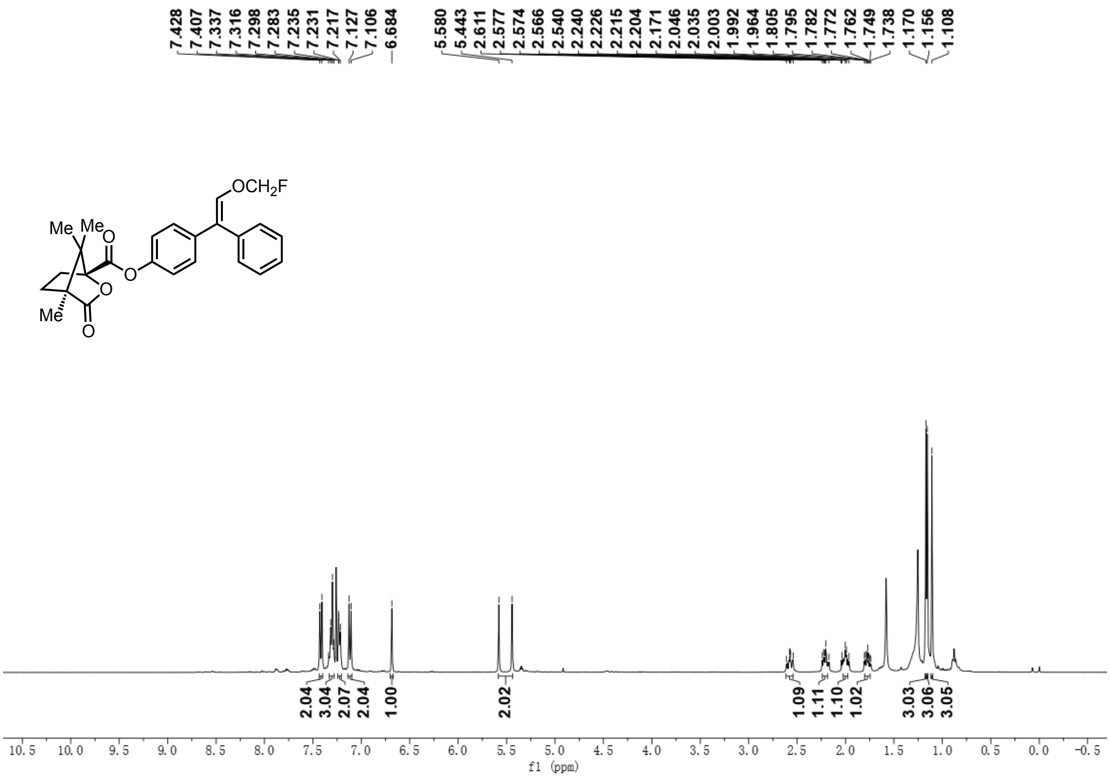
^{13}C NMR Spectrum of Compound **45** (151 MHz, $CDCl_3$)



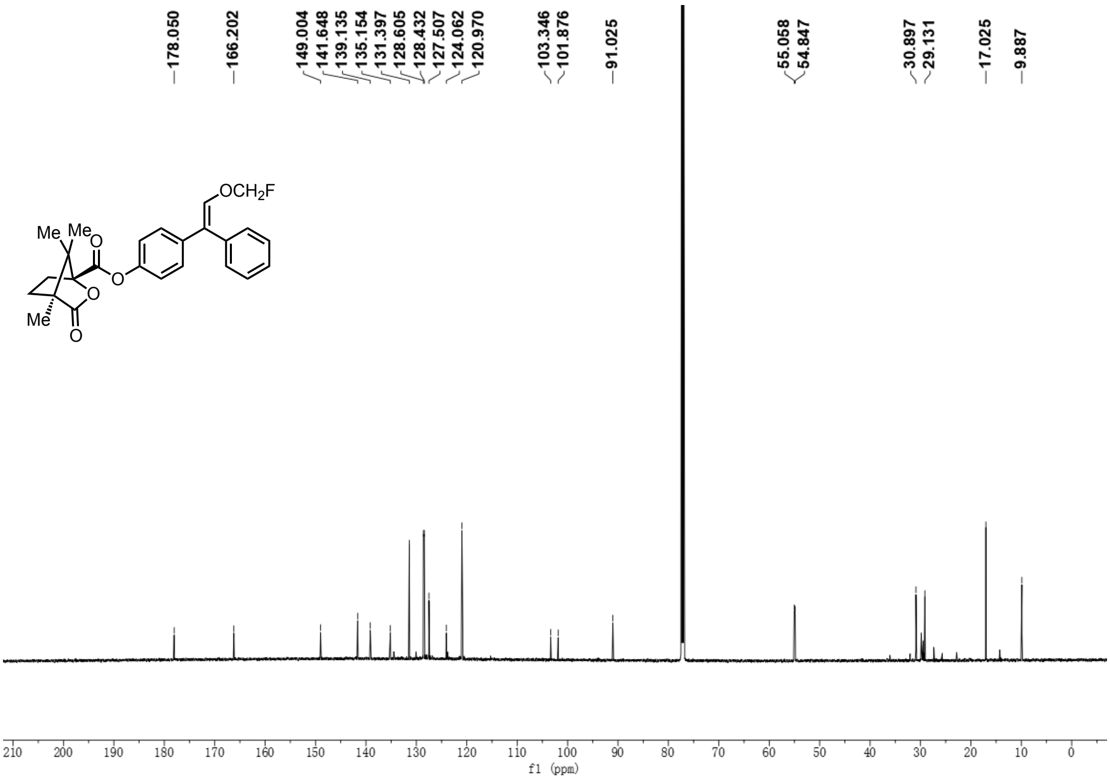
^{19}F NMR Spectrum of Compound **45** (376 MHz, $CDCl_3$)



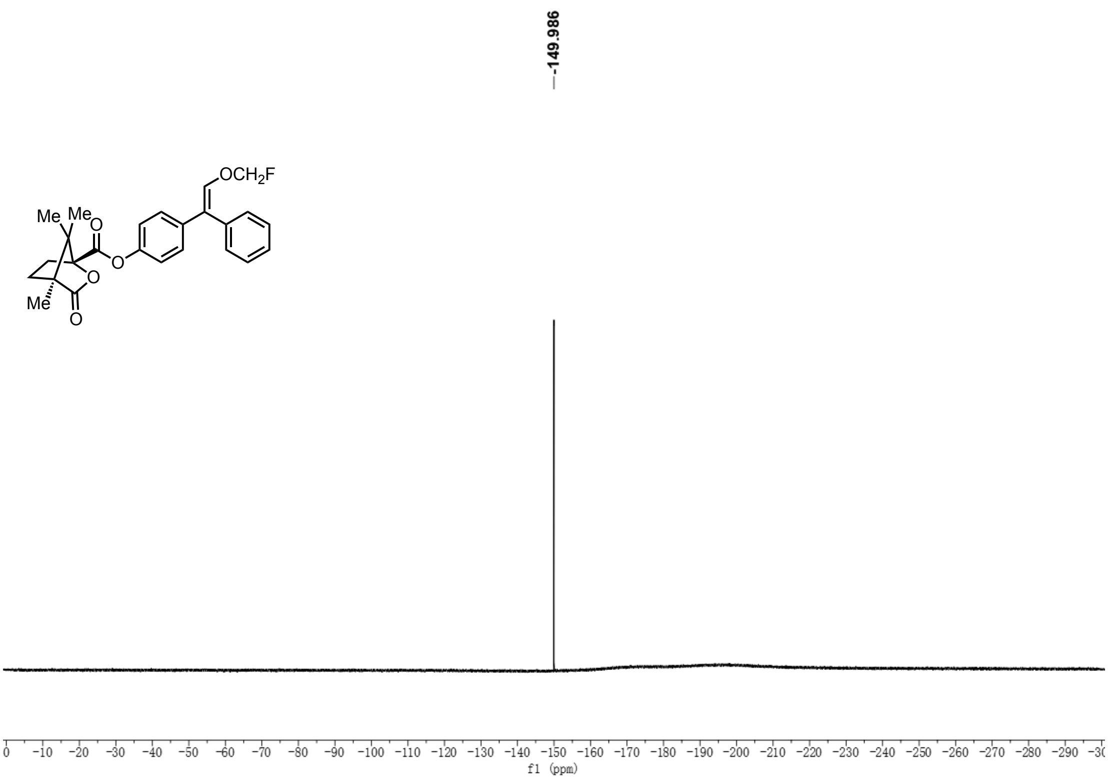
^{1}H NMR Spectrum of Compound **46** (400 MHz, $CDCl_3$)



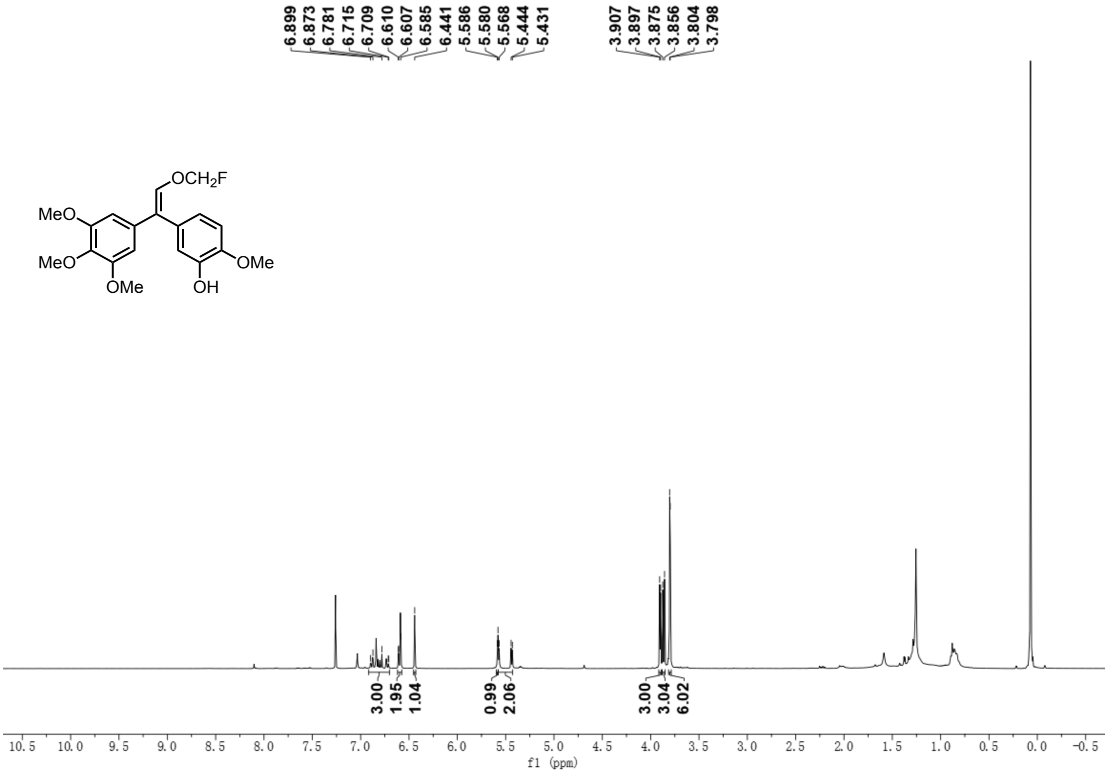
^{13}C NMR Spectrum of Compound **46** (151 MHz, $CDCl_3$)



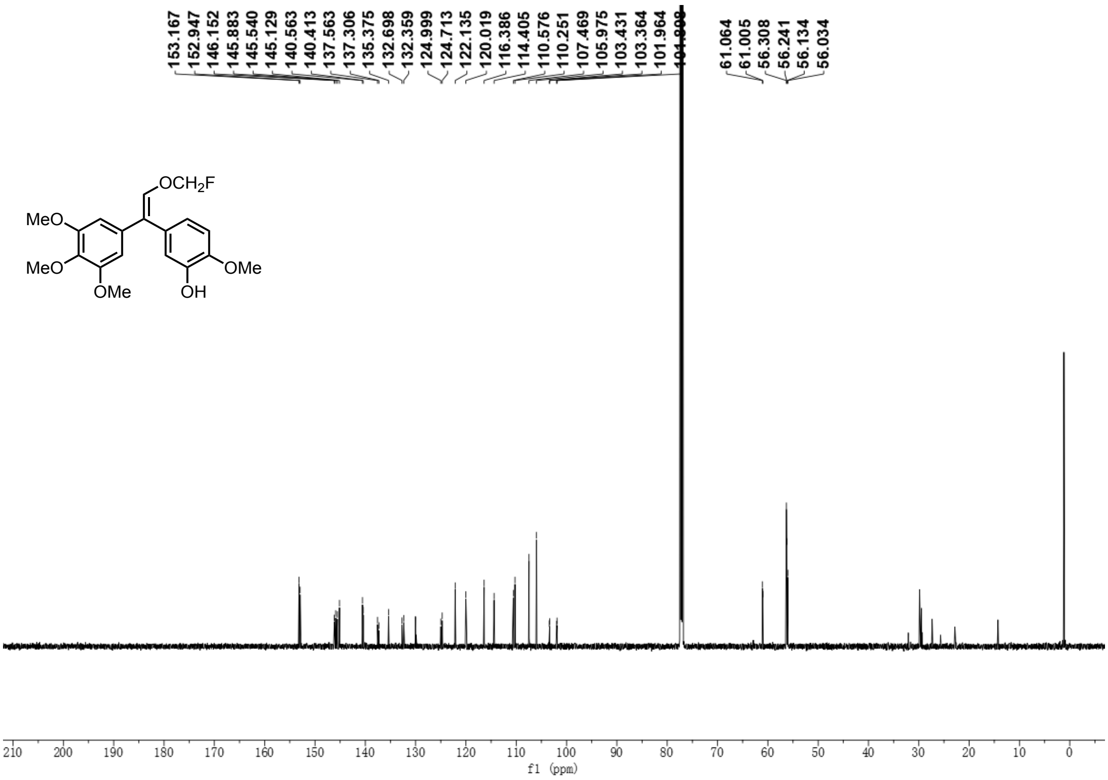
^{19}F NMR Spectrum of Compound **46** (376 MHz, $CDCl_3$)



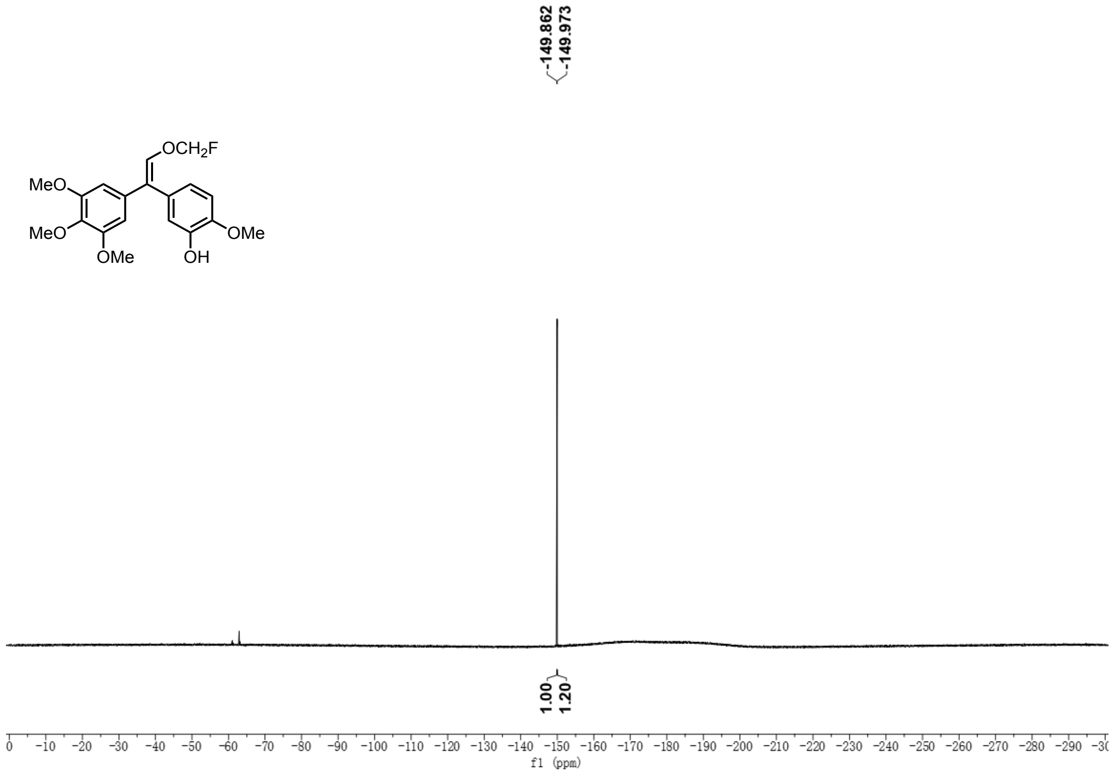
^{1}H NMR Spectrum of Compound **47** (400 MHz, $CDCl_3$)



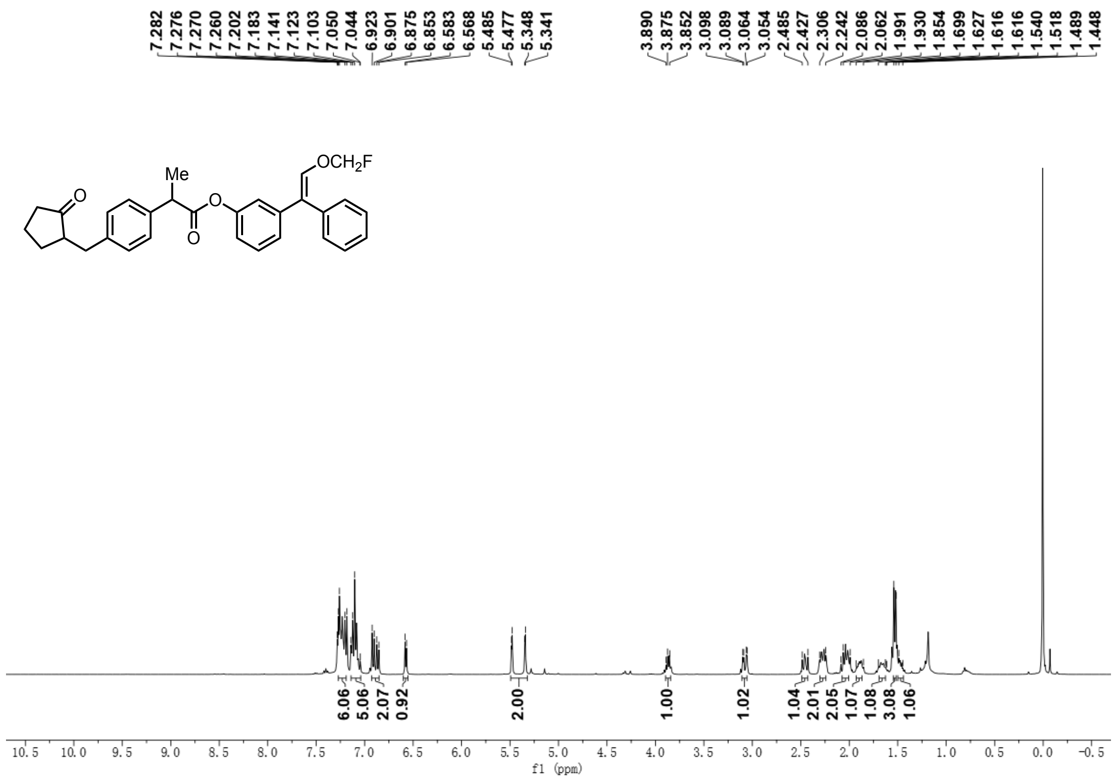
^{13}C NMR Spectrum of Compound **47** (101 MHz, $CDCl_3$)



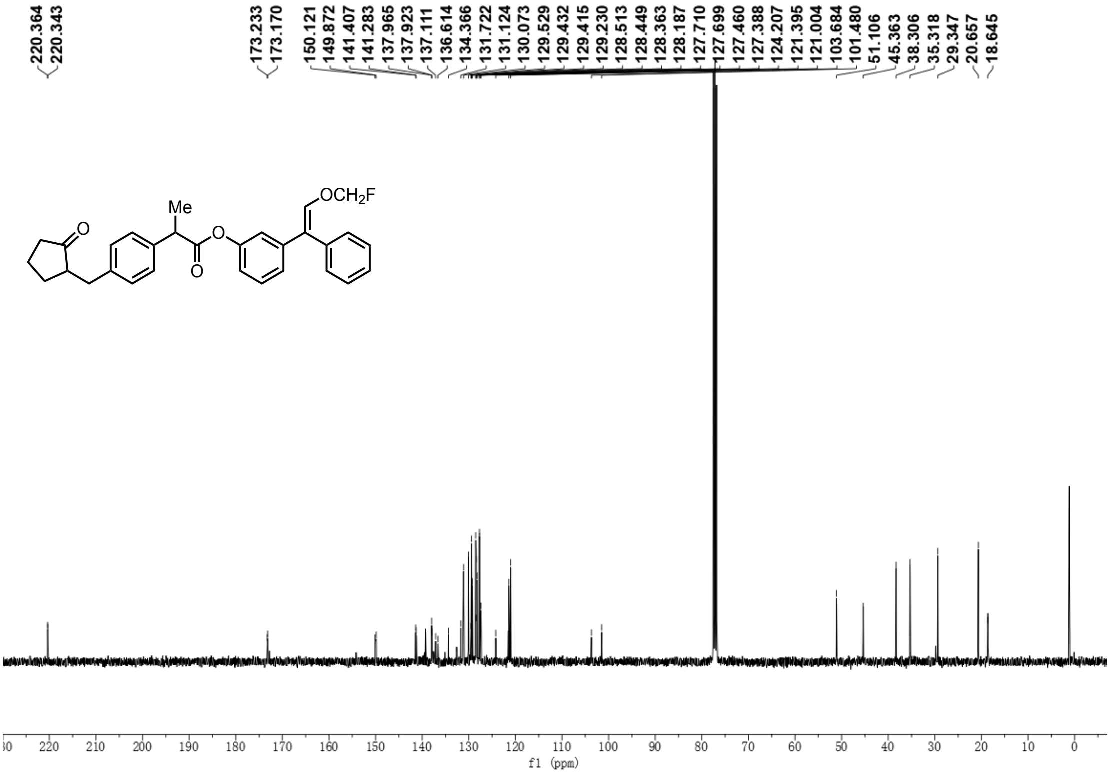
[19]F NMR Spectrum of Compound **47** (376 MHz, $CDCl_3$)



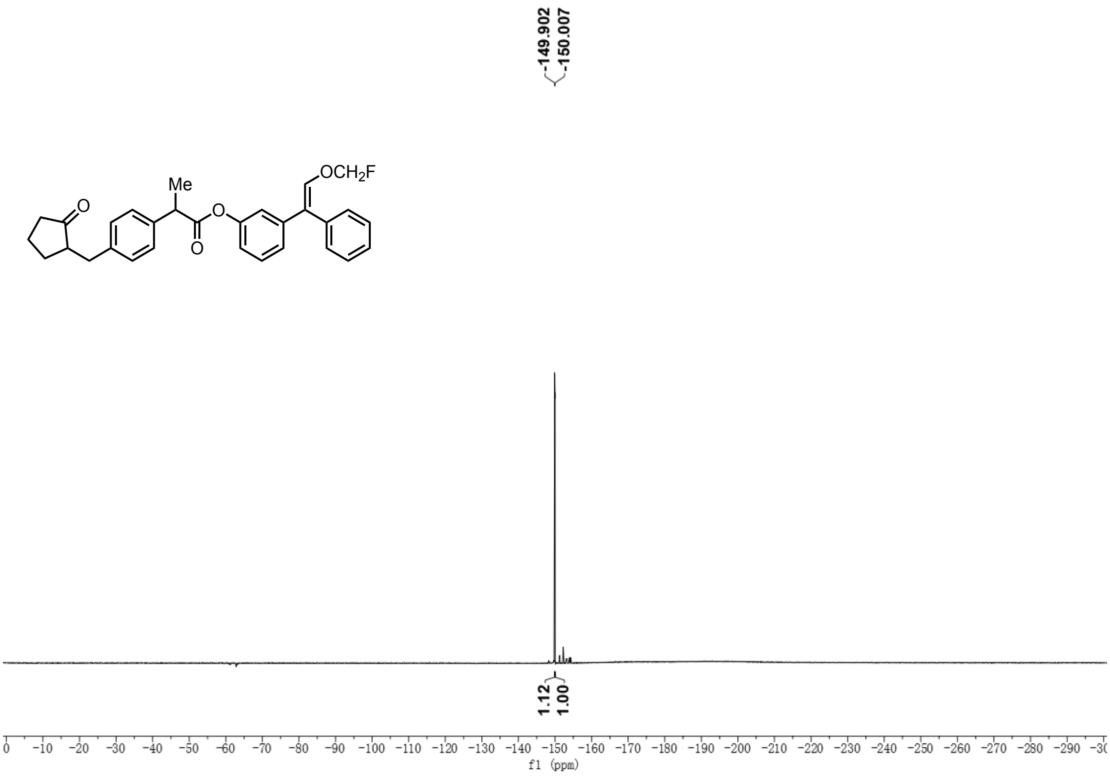
[1]H NMR Spectrum of Compound **48** (400 MHz, $CDCl_3$)



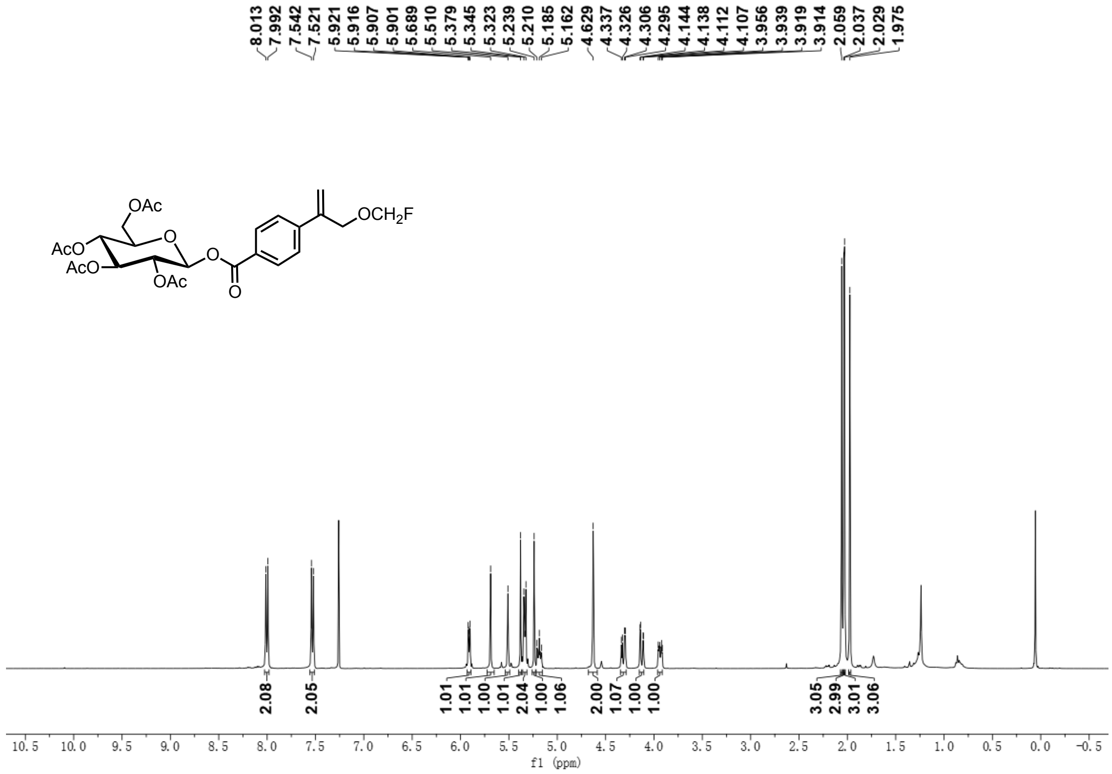
^{13}C NMR Spectrum of Compound **48** (101 MHz, $CDCl_3$)



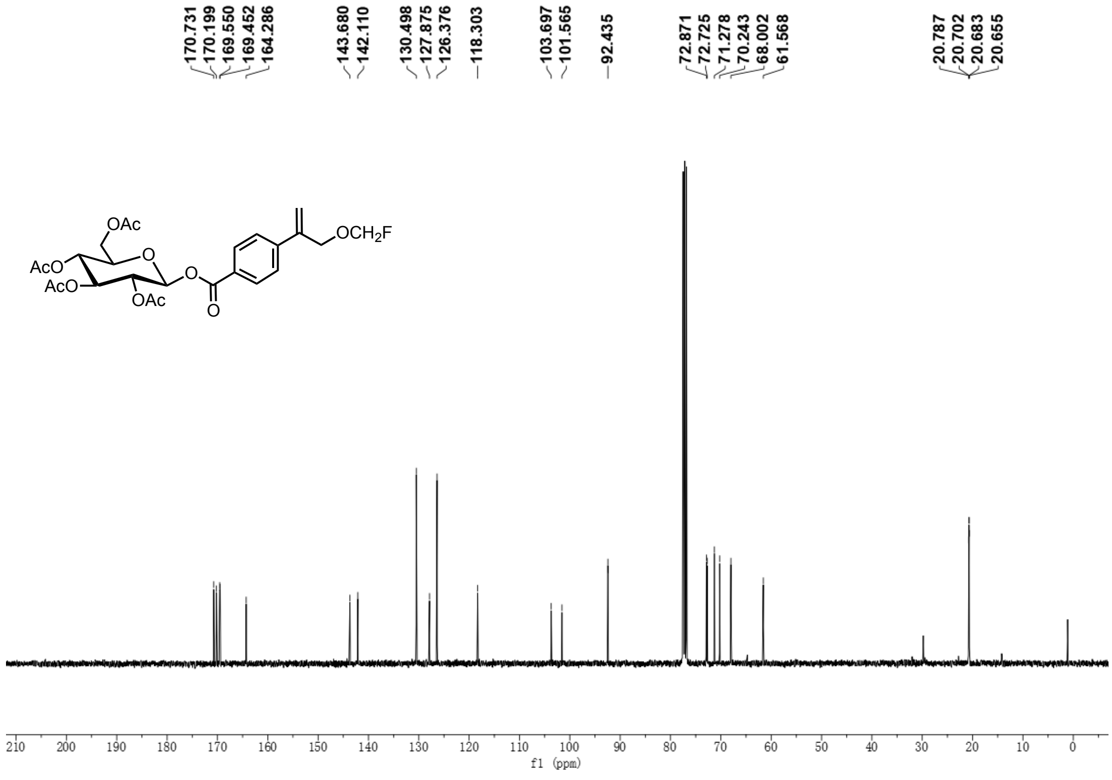
^{19}F NMR Spectrum of Compound **48** (376 MHz, $CDCl_3$)



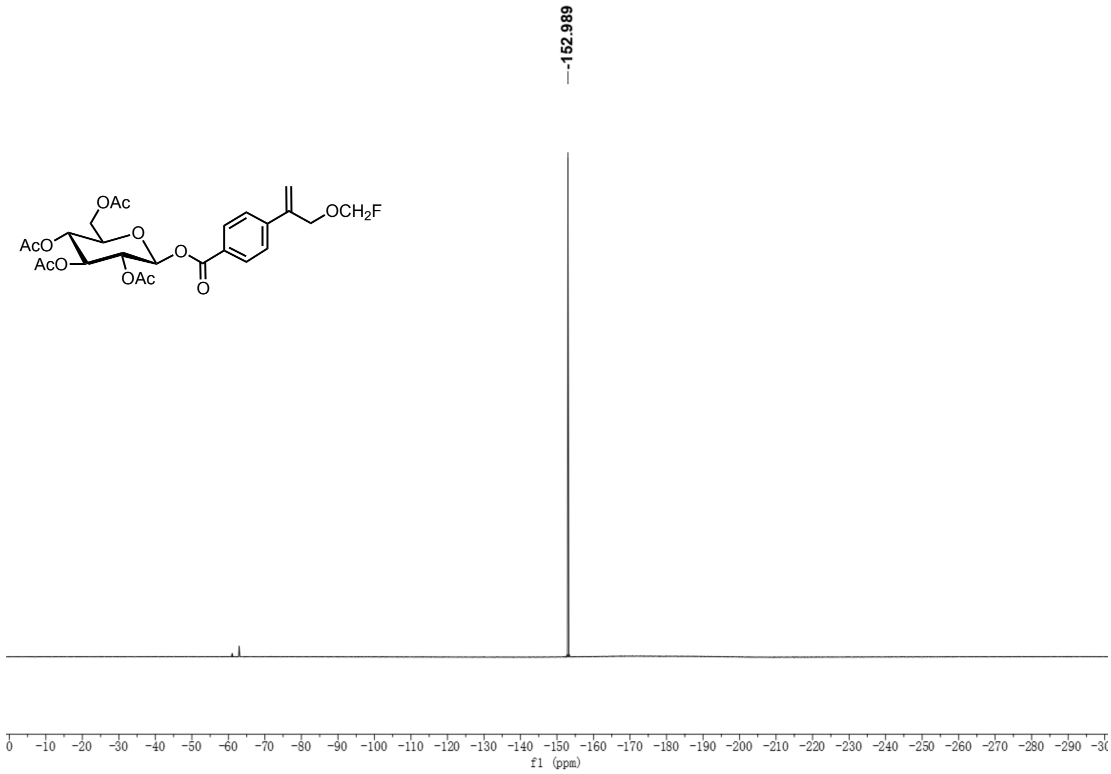
^{1}H NMR Spectrum of Compound **49** (400 MHz, $CDCl_3$)



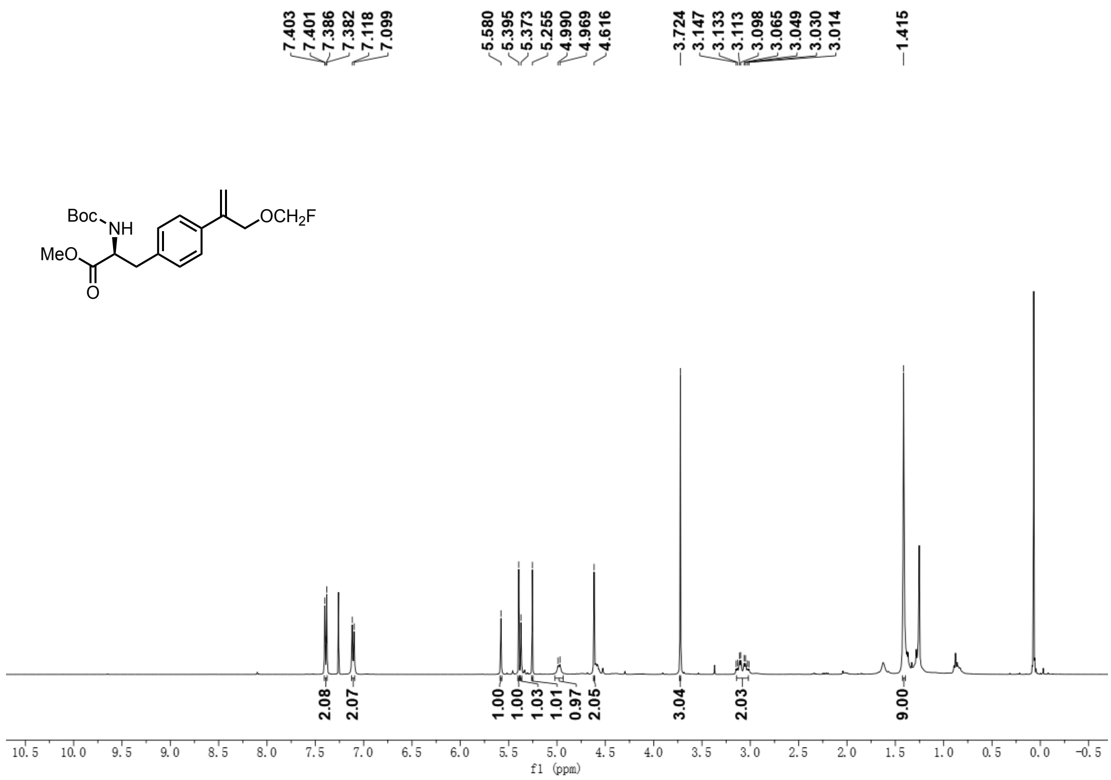
^{13}C NMR Spectrum of Compound **49** (101 MHz, $CDCl_3$)



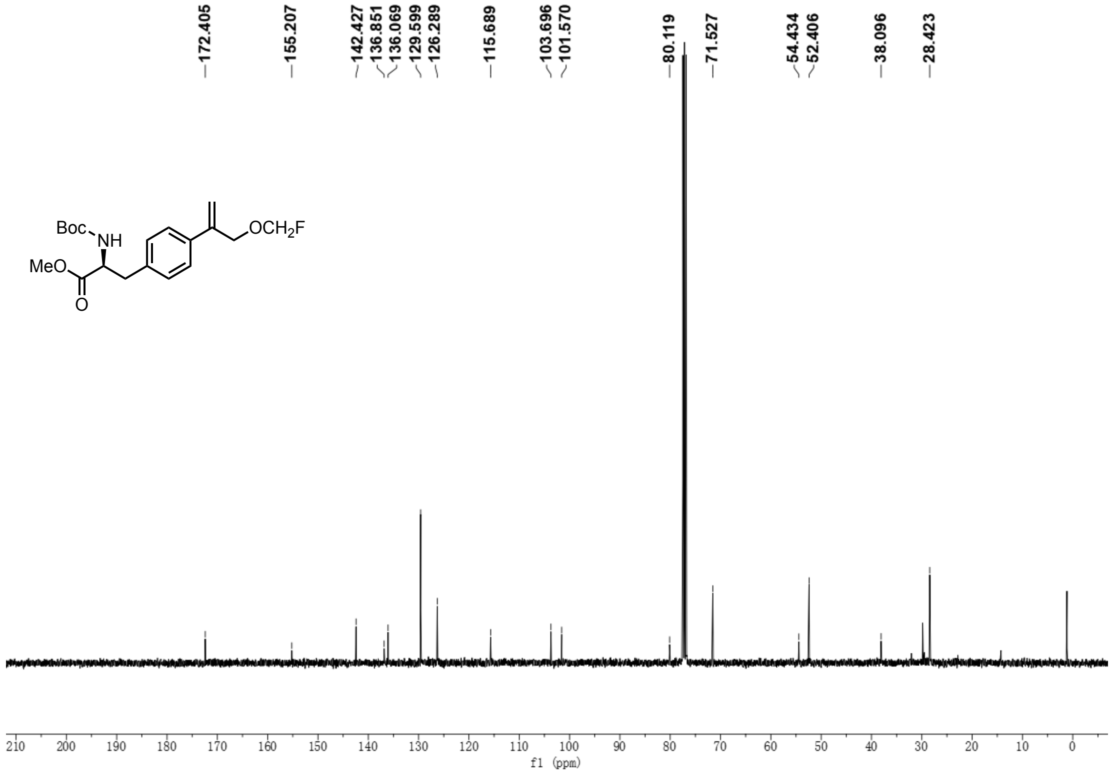
^{19}F NMR Spectrum of Compound **49** (376 MHz, $CDCl_3$)



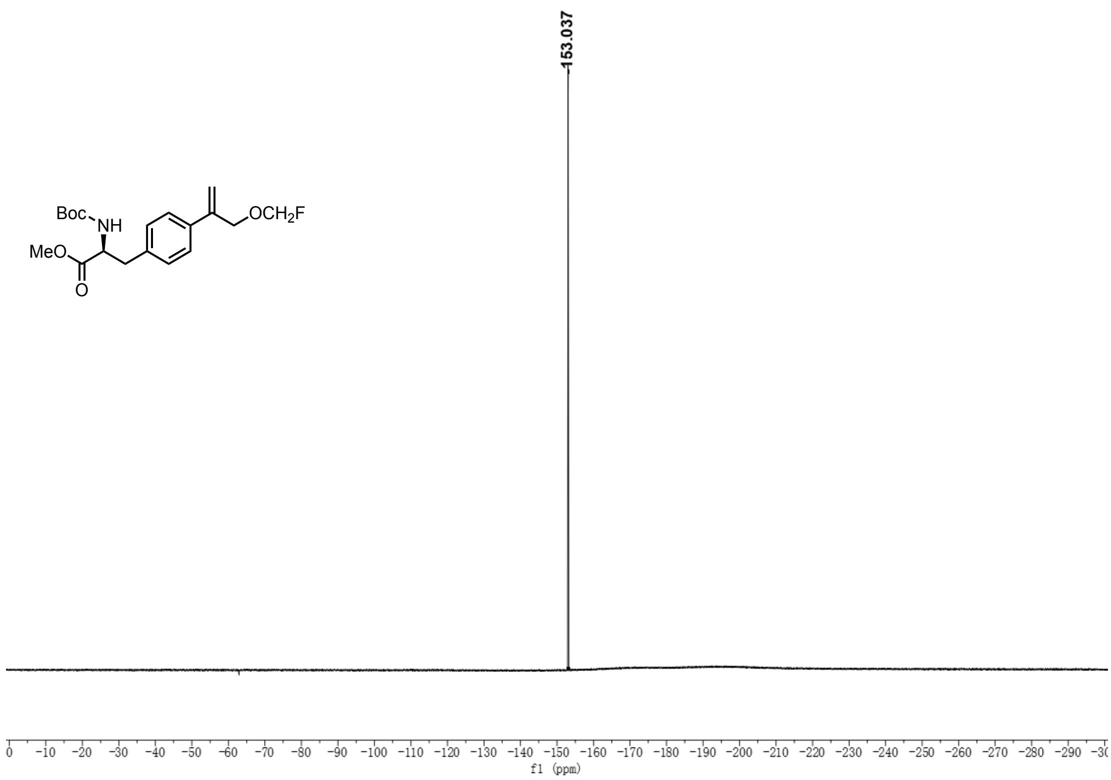
^{1}H NMR Spectrum of Compound **50** (400 MHz, $CDCl_3$)



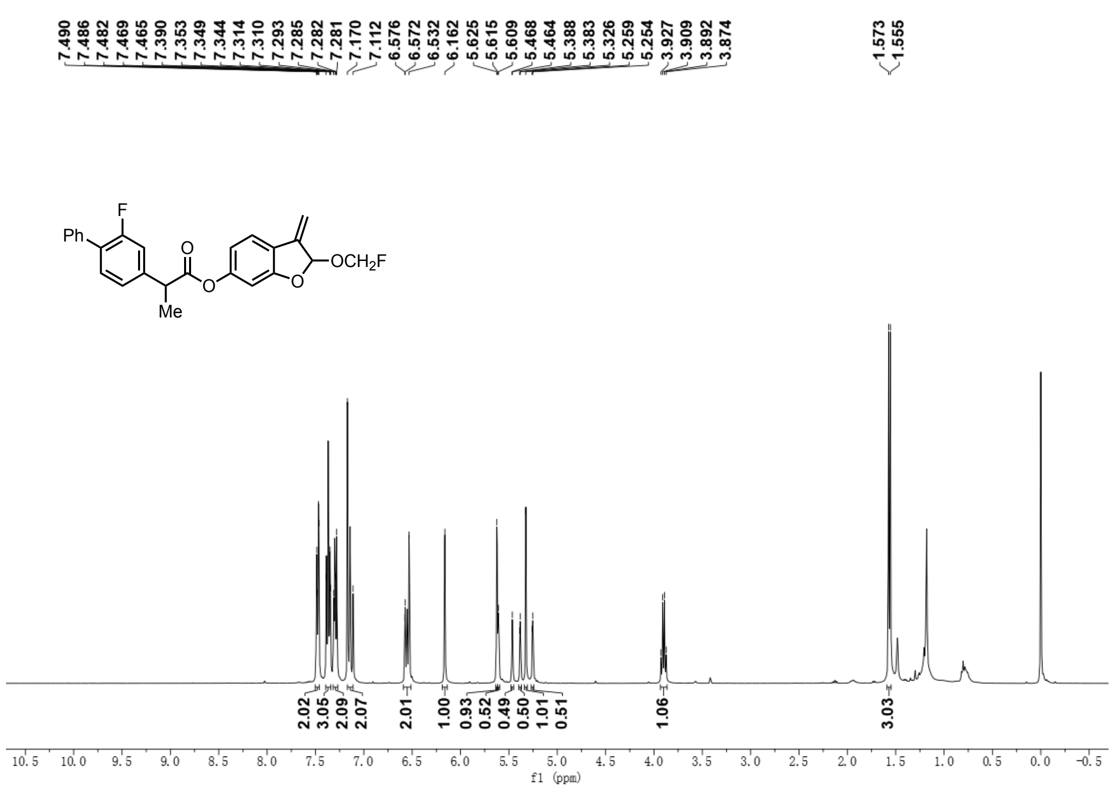
^{13}C NMR Spectrum of Compound **50** (101 MHz, $CDCl_3$)



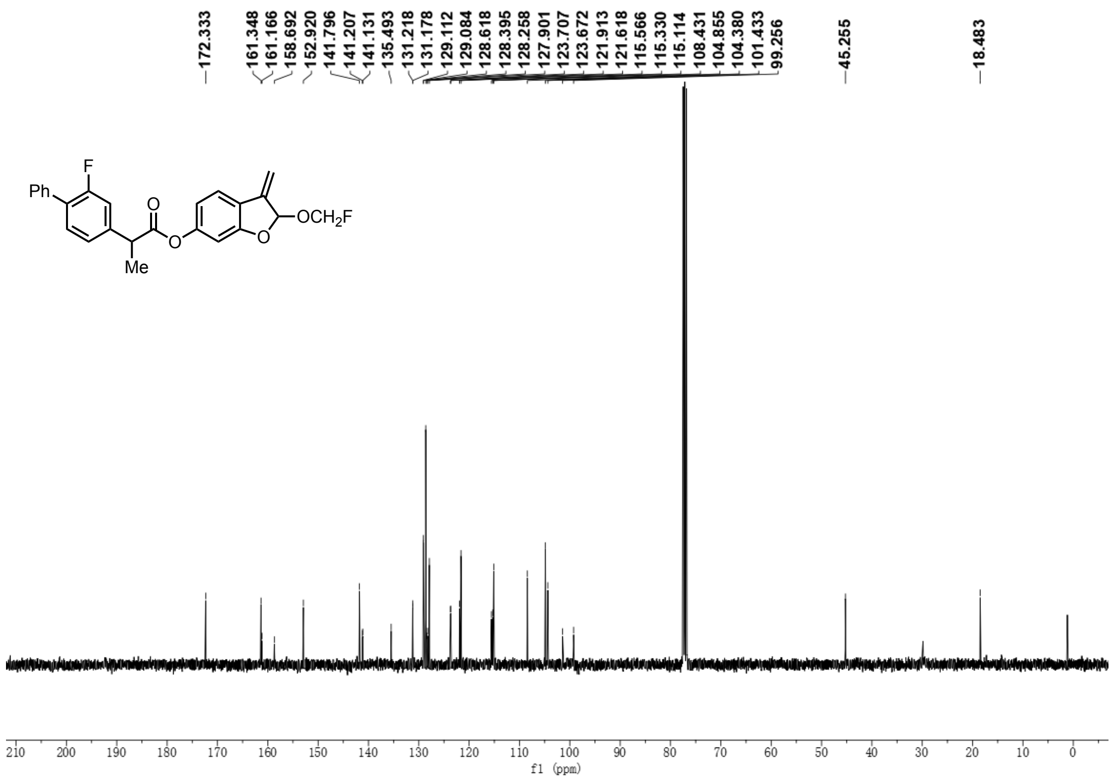
^{19}F NMR Spectrum of Compound **50** (376 MHz, $CDCl_3$)



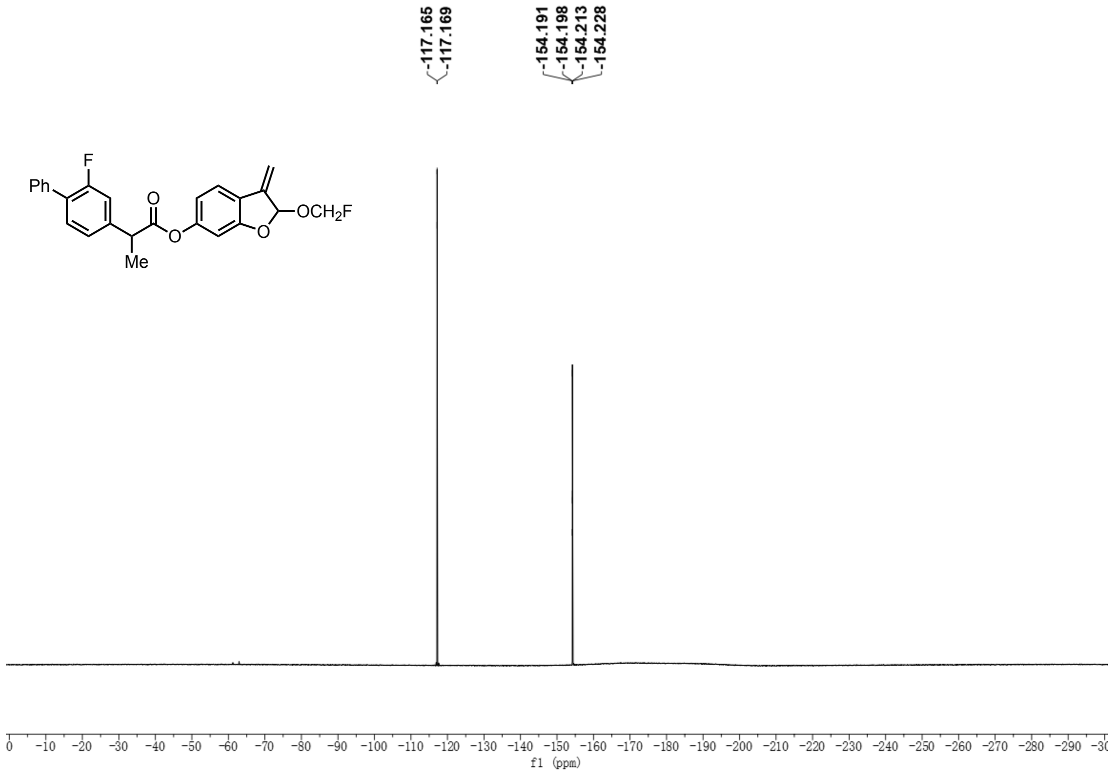
^{1}H NMR Spectrum of Compound **51** (400 MHz, $CDCl_3$)



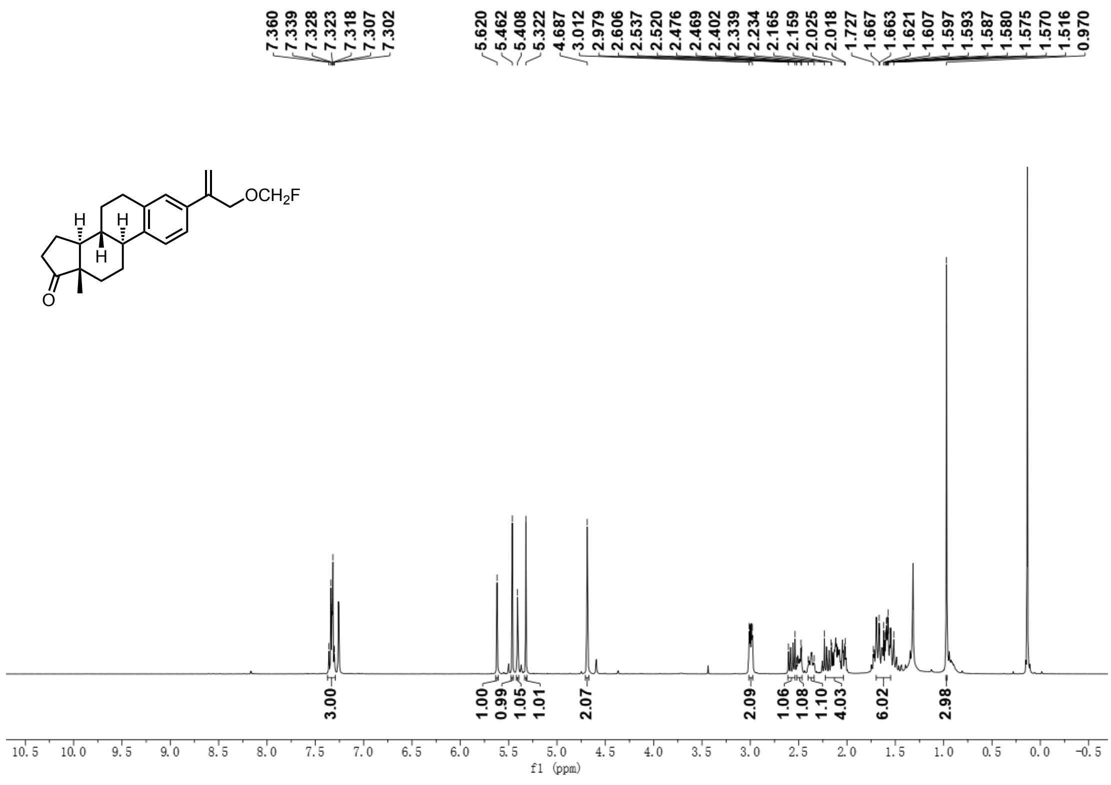
^{13}C NMR Spectrum of Compound **51** (101 MHz, $CDCl_3$)



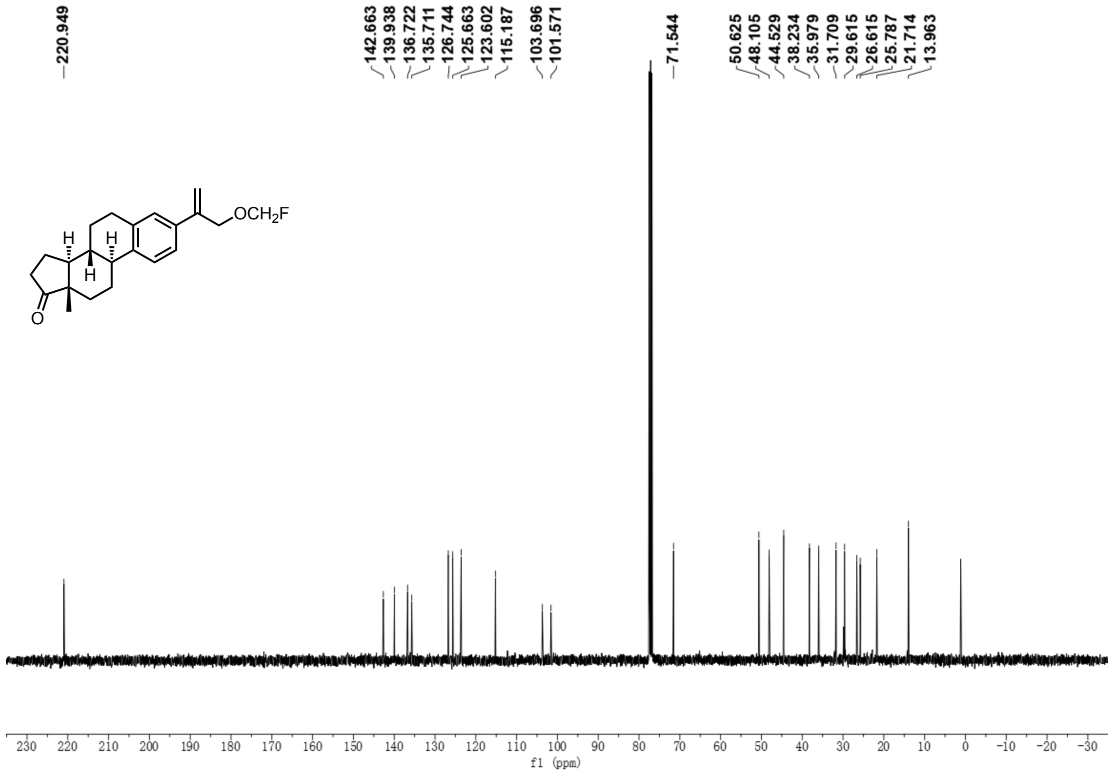
^{19}F NMR Spectrum of Compound **51** (376 MHz, $CDCl_3$)



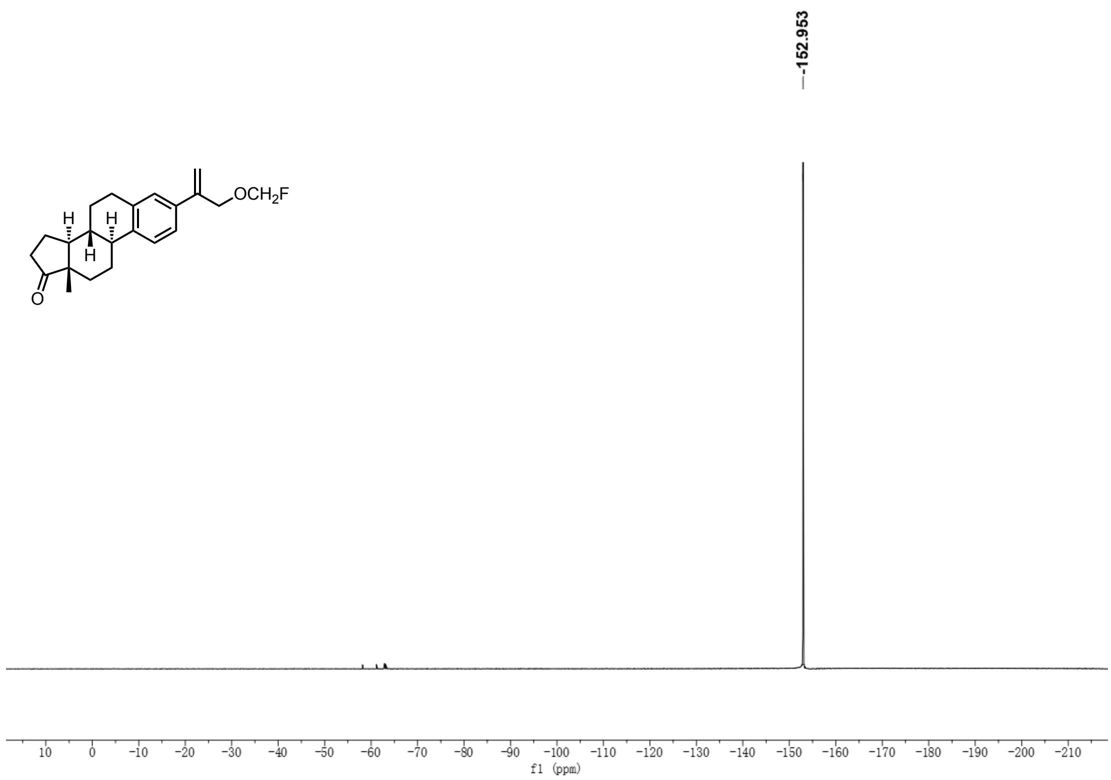
^{1}H NMR Spectrum of Compound **52** (400 MHz, $CDCl_3$)



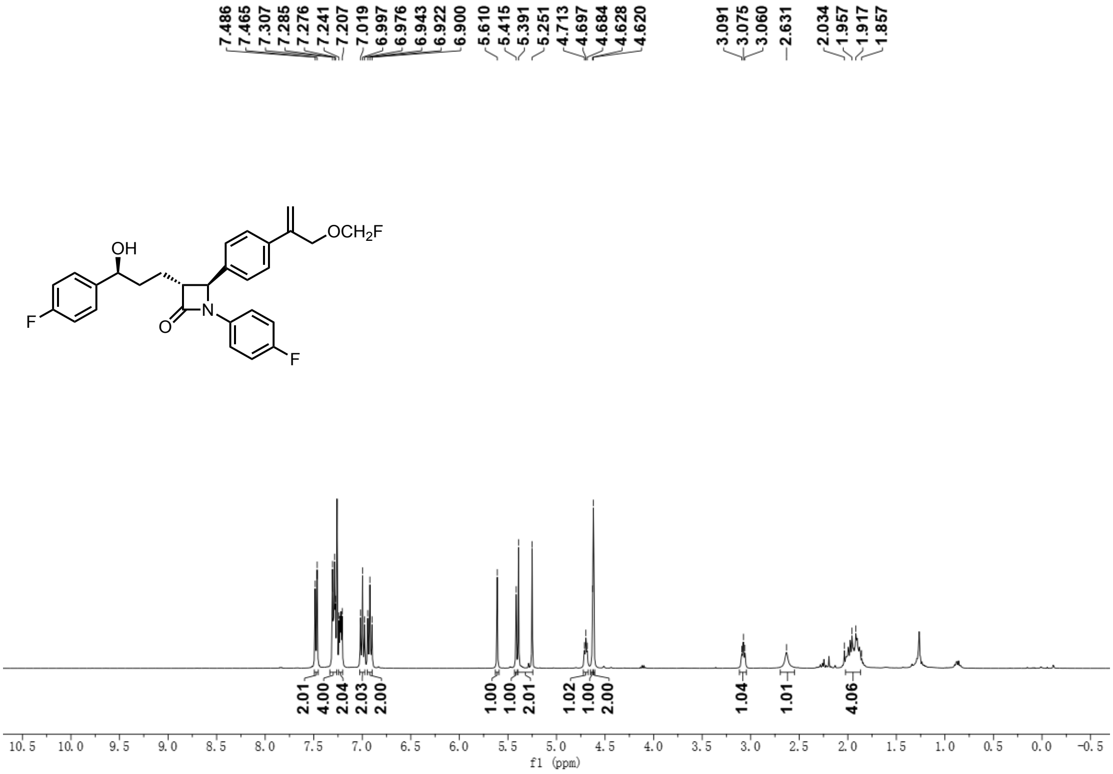
^{13}C NMR Spectrum of Compound **52** (101 MHz, $CDCl_3$)



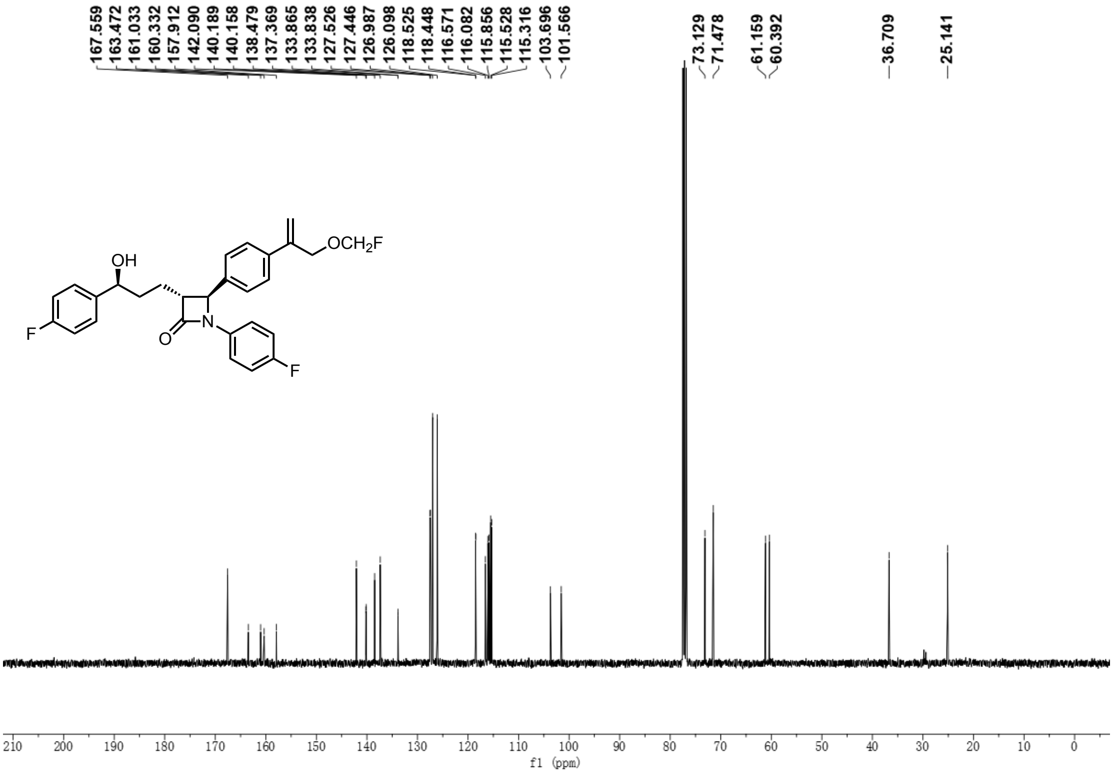
^{19}F NMR Spectrum of Compound **52** (376 MHz, $CDCl_3$)



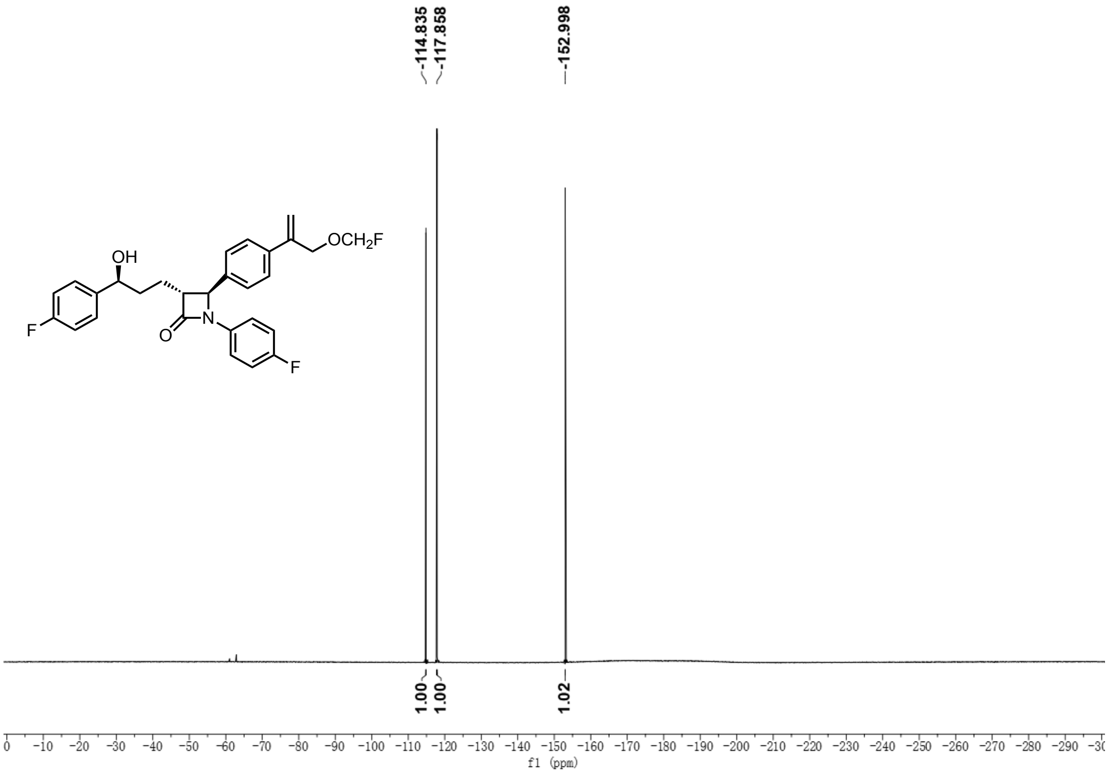
[1]H NMR Spectrum of Compound **53** (400 MHz, $CDCl_3$)



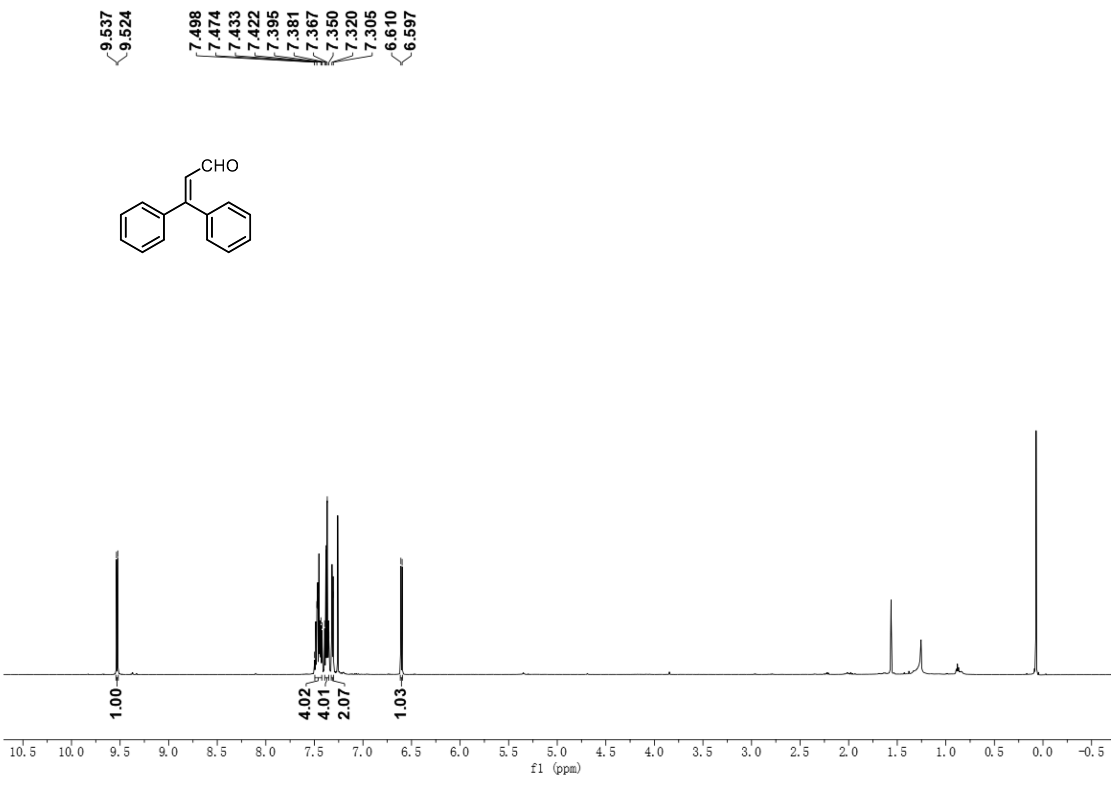
[13]C NMR Spectrum of Compound **53** (101 MHz, $CDCl_3$)



[19]F NMR Spectrum of Compound **53** (376 MHz, $CDCl_3$)



[1]H NMR Spectrum of Compound **3’** (600 MHz, $CDCl_3$)



^{13}C NMR Spectrum of Compound **59** (151 MHz, $CDCl_3$)